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THE

PHYSICAL REVIEW.

THE MEASUREMENT OF HEAT AND THE SCOPE OF CARNOT'S PRINCIPLE.

By Arthur C. Lunn.

Synopsis.—This paper outlines a symmetric form of exposition of the principles of thermodynamics made possible through recognizing on a parity from the outset the two kinds of conservation naturally called after Black and Carnot, each of which is physically valid under proper conditions, and which lead to the energy and entropy scales of measurement of heat; thus exhibiting both of these, together with the thermodynamic scale of temperature, as calorimetric concepts. In the two parts of the paper are given respectively an experimental and a deductive treatment.

In part I. the experimental meaning of conservation is considered in terms of certain conditions of consistency; first in connection with single-temperature transfers of heat, where those conditions underlie the uniqueness of meaning of an arbitrary scale of heat for various temperatures; second in connection with passages of heat between bodies at different temperatures, which reveal the dual nature of a quantity of heat, here illustrated by some analogies.

In part II. are investigated the deductive consequences of Carnot's hypothesis of the universal ratio of efficiency. With only the single-temperature conservation of heat assumed to be known experimentally (probably the mildest basis on which this principle is intelligible), it is shown that there follows practically the entire theory of reversible thermodynamics, in particular the existence of thermal energy and entropy and the equivalence of thermal energy and work.

SINCE the time when the basic principles of thermodynamics were given a standard form, chiefly by Clausius, Kelvin and Rankine, it has become customary not only to speak of "first" and "second" laws but to adopt a corresponding order of thought in the development of their more immediate consequences. It is recognized however that the two principles are at least to a certain extent independent, so that an inverse order of development is conceivable; as illustrated for instance by the fact that Kelvin was able, without using the principle of equivalence, to point out the implication in Carnot's theory of a universal or absolute scale of temperature.[1] Moreover, while the principle of equiva-

[1] Kelvin, Camb. Phil. Soc. Proc., June 5, 1848.

lence enters chiefly on an experimental basis, the second law is made to rest to a large extent on an a-priori hypothesis, in the form of Carnot's principle or its equivalent, to be judged by experimental test of its deductive consequences. An unsatisfactory result is that while the notion of thermal energy, already familiar from experimental calorimetry, becomes still more concrete through equivalence to mechanical work, the notion of entropy, introduced by theorem and definition, appears comparatively abstract and difficult of physical interpretation.

Still, this order of ideas is undoubtedly natural in presence of the general understanding that Carnot's original theory, though contributing the invaluable concepts of the reversible cycle and the universal ratio of efficiency, is in contradiction with experiment through assuming the conservation of caloric in the cases contemplated, the substitution in these cases of the principle of equivalence of heat and work having opened the way for the development of thermodynamics in its now classical form. To make the first law intelligible it is of course assumed that the measurement of heat by itself is already on an experimental basis. This is taken to have been accomplished through the processes of calorimetry, as initiated by the pioneer work of Black, which may be said to rest on the hypothesis or fact, according to the point of view, of the conservation of caloric in certain cases of conduction and the like where it is now known to be an essential feature that no mechanical work is done.

It has not escaped notice however that in some ways Carnot's "caloric" shows distinct resemblance to entropy rather than to thermal energy.[1] Detailed examination shows that most of the propositions of Carnot's essay, and of the formulas in Clapeyron's mathematical commentary and Kelvin's "account," [2] though so often called erroneous and even meaningless by commentators, have a meaning and are correct if "caloric" is taken to mean entropy. It is certain therefore that the amount of inconsistency with experimental results supposed to be present in Carnot's theory has usually been exaggerated and its exact nature not clearly set forth. From the point of view to be explained in this paper the only error of importance appears to be that, not realizing the type of conservation required by his theories to be physically distinct from that of Black, he borrowed numerical data obtained on the energy scale and applied them in cases where they should have been given on the entropy scale. For example, at constant volume the capacity of an ideal gas for change of thermal energy is constant but its capacity for change of entropy varies inversely as the absolute temperature.

[1] Callendar, presidential address, Phys. Soc. Proc., 23, 153–189, 1911.

[2] Clapeyron, J. de L'Éc. Pol., 14, cah. 23, 152, 1834. Kelvin, Trans. Ed. R. Soc., XVI., 1849.

One may say then that the hypothesis of conservation of caloric was used effectively by Black and Fourier in cases where one would now say that thermal energy is conserved and entropy increases, while Carnot assumed it for the case of his reversible engine where thermal energy changes but entropy is constant. The parallel though incomplete is unmistakable. It suggests that the whole basis of thermodynamic theory might be recast in a more symmetric form, securing at the same time a more completely experimental setting, by considering from the outset on a parity the two measurable properties of a quantity of heat and the corresponding scales of measurement based on two types of conservation, each valid in the respective class of cases whereby the experimental establishment of the scale is achieved. Such a formulation is attempted in part I. of this paper where the term "quantity of heat" is for convenience used, in a sense more generic than usual, as denoting a relatively primitive concept not really simple, but which rather may be said to bifurcate into the two distinct and more specific concepts, each of which corresponds in the appropriate cases to the respective types of conservation identified by the names of Black and Carnot.

Such a bifurcation during the process of refinement into scientific precision of a primitive and relatively vague concept is by no means a rare event in the history of science, though as in the theory of heat it is often obscured by the continuance in use, to denote one only of the emerging concepts, of a term previously more comprehensive and indefinite. During the formative period of dynamics search was made for an acceptable measure of the amount of motion in a moving body and the controversies led to the appearance of two important and distinct concepts, momentum and kinetic energy; some traces of vagueness of language remain in the Principia of Newton, though technically he chose to restrict the term "quantity of motion" to the first of these. The "degree of electrification" of a body might be taken to include reference to both charge and potential; the coldness of metal on a winter day is an uncertain blend of low temperature and good conductivity; the distinct concepts quantity of heat and temperature arose from the scrutiny of judgments of "hot" and "cold." In a similar way it seems just to use the term "quantity of heat" in a generic sense, to comprise reference in combination to both of the two independent measurable properties, thermal energy and entropy, although since the foundation of calorimetry the expression has come to be restricted to one of them as a matter of custom. Further examples could easily be cited, but for the present purpose the point of view suggested is especially well illustrated by the following example, which will be seen to furnish a rather vivid and far-reaching analogy to the thermodynamic relations.

The term "amount of gas" may be treated as somewhat indefinite, referring to volume or mass or both jointly according to the interpretation intended, as in the specification of percentages in a gaseous mixture. Suppose then an extensible balloon containing air, with attached tube and shut-off permitting control of contents, be allowed to rise through water in which it is immersed. If the shut-off be closed the mass of air is constant while the volume increases; if the contents be allowed to escape at a suitable rate the volume may be kept constant while the mass diminishes. Here mass, volume, depth, pressure in water, atmospheric pressure at surface, correspond respectively to thermal energy, entropy, temperature on some empirical scale, temperature on thermodynamic scale, and temperature of conventional zero above absolute zero.

In the typical case of Black's calorimetry the heat leaving a body A at a certain temperature and that entering another body B at a lower temperature are such that the thermal energies are the same, but the entropy entering B is larger than that leaving A. In the typical case of Carnot's theory, where the transfer of heat occurs by mediation of a reversible engine working in a simple Carnot cycle between the two temperatures, the entropies involved are equal but B receives less thermal energy than A gives up. Thus the justice of the term "conservation of caloric," in two different senses, seems to be exactly the same in the two cases.

The incompleteness of the parallel with respect to other features may also be instructive. In both cases there is known to be conservation of energy, because the variations of mechanical energy in its various forms compensate those of the thermal energy; while there is not yet recognized any physical magnitude whose variations compensate those of the known thermal entropy, so as to allow the formulation of a law of conservation of entropy in some wider sense. Still it is conceivable, as Callendar suggests, that there may be other and equivalent forms of entropy, and especially does there seem to be a chance for speculation on this point in connection with the thermodynamics of radiation. Perhaps also there may be other and independent aspects of heat, beside energy and entropy, whose conservation could be established in some experimentally intelligible sense; for instance in connection with the aggregate result of the molecular Döppler effects, since energy and temperature alone do not determine spectrum of radiation if the black body condition be not imposed. Such novel aspects or magnitudes could probably not be sifted out by the study of bodies, like fluids in gross, whose state depends on only two independent thermodynamic coördinates.

As underlying the interpretation of thermal measurements the notion

of conservation or equivalence appears in various forms. These may be analyzed in terms of three fundamental types, corresponding to the following three elementary cases of experimental comparisons: (1) comparison of quantities of heat entering or leaving different bodies at the same temperature, (2) comparison of quantities of heat at different temperatures, (3) comparison of heat with other physical entities, especially completely available energy in some form.

The treatment given in Part I. shows that on the basis of the first two only, including the suggested dual aspect of the second, it is possible to exhibit entropy as well as thermal energy as a calorimetric magnitude, thus reaching a more symmetric experimental setting than the familiar forms of the theory. The equivalence of thermal energy and work is then introduced as an additional experimental result, while the existence of an analogous non-thermal equivalent for thermal entropy appears merely as a question.

As an alternative development a symmetrically deductive treatment is given in Part II. Here the only experimental comparisons assumed are of the type (1) above, while Carnot's hypothetical principle of the universal efficiency function is stated as a postulate. The existence of thermal energy and entropy, identifiable with the experimental concepts, is deduced, so that for reversible processes there follow both first and second laws as commonly understood. Thus, on what appears to be a minimum basis of experiment sufficient to make the measurement of heat an intelligible notion at all, Carnot's principle alone proves to be an adequate hypothetical basis for the entire general theory of the thermodynamics of reversible processes, having in particular the principle of equivalence of heat and work as a corollary. Distinct indications of the possibility of such a conclusion will be found in the apparently little known memoir by Reech,[1] in which the development is such that it can be specialized further by assuming either conservation of energy or conservation of caloric, considered as mutually incompatible. Results partially similar to those now obtained will also be found in the recent papers by Larmor and Raveau,[2] dealing with Carnot's principle apart from the principle of equivalence. Some reference will be made later to corresponding features in these papers, but the detailed comparison will be left to the reader.

PART I. EXPERIMENTAL SETTING.

Passing over the complex detail of experimental methods and the involved questions presented to the experimenter's judgment in the

[1] Reech, Liouv. J., ser. 1, 18, 357–568, 1853.

[2] Larmor, Roy. Soc. Proc., 94, 326–339, 1918. Raveau, C. R., 167, 20–23, July 1, 1918.

attempt to sift from among secondary or accidental aspects the main elements of the phenomena to which attention is to be directed, it will be sufficient here merely to notice certain salient features of the results, that either have been obtained or with appropriate experiments would be obtained if thermodynamics in its familiar form is valid. As to thermometry, it will be supposed that means have already been secured for identifying particular physical temperatures, and that the various temperatures are known to form a simple or linear ordinal series, in connection with which the terms "higher" and "lower" have their usual meaning. If data are to be transcribed with the aid of some numerical specification of temperature it will be understood that the physical order of rising temperature corresponds to the order of increasing values of the index variable t, without implying any initial physical interpretation for equality or comparison of intervals in different parts of the scale. In most cases it will be clear that t could be understood merely as some symbol of identification, not necessarily numerical.

Viewing then to begin with as merely tentative the notion that heat can be measured at all, one may ask what there is in the experimental processes developed and the results reached to show that heat possesses properties truly measurable, and such that the results of measurement can be described justly in terms of the standard language of equivalence and conservation. In the main the answer is that in all the types of comparison involved in thermal measurements there appears a certain unanimity in satisfying what may be called conditions of transitivity, or conditions of consistency as they become in the phrasing suggested by the point of view represented in the notion of equivalence; conditions as to sense or algebraic sign, and as to value or measure. Between these two kinds also there is a certain formal analogy that needs no attention here. It is because these conditions are satisfied that it is possible to formulate the meaning of a "quantity of heat" as something having value and sign. This formulation, found by experience to be both just to the facts and convenient in describing them, is best thought of as occurring in connection with observation of such variations in physical properties, supposedly due to thermal processes, as affect features already known to admit of algebraic representation, like length, volume, density, mass of a particular phase. Both kinds of conditions of course appear in a variety of forms, corresponding to the various kinds of bodies involved and the various kinds of thermal exchange between them.

In language made unconventional in order to avoid specific terms already adopted as technical, the conditions of sense may be described as referring to a distinction between some change called "waxing" and its

opposite "waning," the terms bearing various meanings for various bodies or kinds of change. Suppose then in each single experiment of a set a certain pair of bodies in thermal exchange, all other bodies being found unaffected in certain prescribed respects. With A and B in exchange let A vary in a way called waxing by definition, then what B does may be called waning; in exchange with C suppose B waxes, then what C does is naturally called waning; no more definition being needed, there is content of fact in saying that with A and C in exchange if A waxes C wanes. In case n bodies were paired off in all possible ways there would be one arbitrary definition, $n - 1$ definitional pairings, and $(n - 1)(n - 2)/2$ pairings for test of fact. There are also in connection with processes that can be reversed items of fact to the effect that reversals of sense correspond in the two bodies of a pair. In view also of the number of ways in which the same body may be affected by thermal exchange according to the conditions imposed, it is clear how broad is the justification in fact for speaking of heat as something entering or leaving a body.

The matter of numerical value is closely similar. The magnitudes of corresponding changes in the bodies of a pair are found to be related in some way, and the observed relation for A and C can also be computed from the relations for A and B and for B and C by algebraic elimination. The character of the algebraic process depends on the choice of variables used in transcribing the measurements, the usual case being the multiplication of ratios. With any number of bodies in the set to be compared, a particular one may be chosen to be paired off with each of the others, either to decide on convenient definition of terms or by process of calibration to fix on a suitable choice of variables; then all other pairings give tests of fact. The consistency thus revealed is the ground for speaking of heat as something admitting quantitative estimate.

Whether every type of sequence, or in what sense any particular sequence, of thermal comparisons would satisfy these conditions need not be discussed here; some of the outstanding problems relate to the question whether other and independent quantitative aspects of heat remain to be discovered. The few special types to be mentioned here are actually of the consistent or conservative type, and prove to be sufficient as basis for the theory aimed at. In each case the meaning of the conditions of consistency in sense or sign may be passed over as obvious without comment; the conditions of consistency in value or magnitude will be sufficiently illustrated by the forms that they take in certain standard cases of the three types of comparison listed above.

Comparisons of the first type, of quantities of heat entering or leaving

bodies at the same temperature, lead to the conclusion that all such can be compared among themselves and represented consistently by simple ratios; or in other words that for such single-temperature comparisons a quantity of heat can be considered a simple thing, capable of representation by a single number in terms of any chosen unit belonging to that temperature, regardless of the kind of body concerned or the kind of change produced in it according to collateral conditions imposed. This leads to the introduction of what may be called an empirical or arbitrary scale of heat, including a single specific unit for each temperature, but not implying anything as to the possibility of comparing two quantities of heat when the temperatures are different. An approximate example of such a scale is found in the system of differential calories, according to which the specific heat of water is by definition unity at every temperature. A better example for the purpose is to be found in strictly isothermal processes, especially changes of state, though latent heats of expansion would also serve. Through a suitable variation of pressure the latent heat of transition between liquid and vapor of a single substance could furnish such a scale for a considerable range of temperature.

Consider then a variety of substances such that the respective pressures can be adjusted so that the temperatures of transition agree. In the absence of such adjustment for any two particular substances A and B, suppose thermal exchange between them for a certain time leads to the transformation of the respective masses m_A, m_B, the transition being reversed in both bodies with reversal of sense of the temperature difference. With temperature difference approaching zero the ratio m_A/m_B of corresponding masses approaches a limiting value μ_{AB} to be understood as the ratio of masses transformed in the ideal limiting case of reversible or single-temperature conduction.

The main experimental facts of significance here are then: that the ratio μ_{AB}, depending on the temperature of transition and the nature of the substances, is independent of the absolute mass transformed, and that for the same temperature the various ratios for the various bodies of the set satisfy conditions of transitivity in the form $\mu_{AB}\mu_{BC} = \mu_{AC}$. This multiplication of ratios is of course not merely a mathematical identity, though conveniently given a mnemonic form as such, the meaning being that if m_A be the same in the experiments (AB) and (AC) and m_B the same in experiments (AB) and (BC) then as an experimental fact m_C will be the same in (AC) and (BC). The fact that the ratio of masses is characteristic suggests that a quantity of heat can be numerically indexed as proportional to the mass transformed of some particular substance.

The conditions of consistency in the compounding of the ratios furnish one instance of the universal consistency in the comparison of various temporary units of heat belonging to the same temperature, though in general the mathematical form varies. In such facts is found the experimental basis for the effective accuracy of the language of conservation, according to which for example one can speak of a quantity of heat going from A to C either directly or through B. In the sense illustrated it will now be supposed that the meaning of a quantity h of heat at a temperature t has been established. Certain familiar terms, like the differential specific heat dh/dt, become intelligible in connection with any definite choice of the scales of heat and temperature.

For the second type or multiple-temperature comparisons consider a set of bodies or reservoirs maintained at their respective various temperatures, any certain three of which, such as will be referred to, being labelled in descending order as t_1, t_2, t_3. The two distinct forms of conservation already alluded to will then appear in connection with thermal exchange between these bodies of the two kinds naturally named after Black and Carnot.

The first form, fundamental in classical calorimetry, occurs when the bodies communicate by pure irreversible conduction or radiation, or by the mediation of some mechanism such that the various quantities of heat are related in the same way. The second occurs when the bodies communicate by mediation of a reversible engine working in Carnot cycles between the two temperatures. In the first case suppose h_1 units of "t_1-heat" leave the first body and h_2 units of "t_2-heat" enter the second body; let $h_1/h_2 = b_{12}$. Similarly in the second case, the two quantities of heat being h_1' and h_2', passing when the engine is on the isothermals, put $h_1'/h_2' = c_{12}$.

Now calorimetry as ordinarily understood, or the measurement of heat by itself in Black's sense, rests largely on the experimental facts: that b_{12} depends on the two temperatures only save for its obvious variation according to the choice of the scale of heat; and that in terms of any one scale of heat the ratios for various pairs of bodies satisfy the condition $b_{12}b_{23} = b_{13}$. But according to standard thermodynamic theory it is indirectly understood to be a fact, and by suitable apparatus could doubtless be shown to be experimentally verifiable with considerable directness, that the ratios c_{12} and the like satisfy similar conditions. The fact that the b's are independent of the physical nature of the reservoirs and the character of the changes produced in them is paralleled by the fact of a similar independence on the part of the c's of the properties of the reservoirs and the nature of the mediating engine.

Thus in each case there is complete ground for concluding that there is a sense in which the heat is conserved in passing out of one reservoir and into the other. But it is also to be understood as found experimentally that $b_{12} < c_{12}$; accordingly the two types of conservation must be physically distinct.

Thus a quantity of heat h, entering or leaving a body at temperature t, exhibits two distinct measurable properties, thermal energy and entropy, whose measures q and s are related to the empirical measure of heat by equations of the form

$$q = hB(t), \qquad s = hC(t),$$

where the reducing factors $B(t)$, $C(t)$, appropriate to any particular scale of heat, are determined, except for an arbitrary constant factor in each depending on the choice of the units for q and s, by the conditions

$$B(t_2)/B(t_1) = b_{12}, \qquad C(t_2)/C(t_1) = c_{12},$$

which are the transcription of the equality of q_1 and q_2 in the Black process and of s_1 and s_2 in the Carnot process.

A change of the scale of heat can be represented by putting $h = h'\rho(t)$ where $\rho(t)$ is the ratio of the new to the old unit of t-heat; the corresponding new reducing factors are then $\rho(t)B(t)$ and $\rho(t)C(t)$, supposing the units of q and s not altered. In particular ρ could be taken as the reciprocal of either B or C, thus reducing the arbitrary scale of heat to the energy or entropy scale.

If by definition $T(t) = B(t)/C(t)$, then in view of the inequality $b_{12} < c_{12}$, which gives $B(t_1)/C(t_1) > B(t_2)/C(t_2)$ it follows that $T(t)$, the absolute or thermodynamic scale of temperature thus shown to exist, is a monotonic increasing function of the physical temperature, is independent of the choice of the scale of heat, and is determinate except for a constant factor depending on the units of q and s, whose values for the same quantity of heat are related by $q/s = T(t)$.

With the aid of this scale of temperature the two cases may then be epitomized as follows, the different equations in each set being equivalent but suggesting different interpretations:

$$B: \quad q_1 = q_2; \quad s_1T_1 = s_2T_2; \quad (s_2 - s_1)/s_1 = (T_1 - T_2)/T_2;$$
$$(s_2 - s_1)/s_2 = (T_1 - T_2)/T_1; \quad s_2 - s_1 = q_1(1/T_2 - 1/T_1);$$

$$C: \quad s_1 = s_2; \quad q_1/T_1 = q_2/T_2; \quad (q_1 - q_2)/q_1 = (T_1 - T_2)/T_1;$$
$$(q_1 - q_2)/q_2 = (T_1 - T_2)/T_2; \quad q_1 - q_2 = s_1(T_1 - T_2).$$

To each equation valid in one case there corresponds one valid in the other case obtained by interchanging q with s and T with $1/T$. For

example there are two instances of the Carnot simile of the waterfall: in C the thermal energy $s(T_1 - T_2)$ is lost when entropy s falls through the temperature difference $T_1 - T_2$, while in B entropy $q(1/T_2 - 1/T_1)$ is generated when thermal energy q rises through the difference of the reciprocals of the temperatures. In each case the statement of the condition of conservation in terms of the non-conserved quantity gives a kind of calorimetric aspect of the familiar Carnot ratio and its dual. The universality of these ratios, as depending on the temperatures only, is a consequence of the universality of the ratios b and c mentioned above, which is what makes it possible to abstract the notions of thermal energy and entropy out of the properties of particular bodies.

Up to this point only heat entering or leaving a body has been spoken of. But the conservation of entropy in the Carnot process leads by a familiar reasoning to the conclusion that all reversible transformations connecting two states of the working substance must agree in the amount of entropy absorbed, this amount being the integral of the calorimetric expression for ds in terms of reversible changes of the temperature and other observable properties of the body. The existence of a function of state properly called the entropy of the body is thus recognized, in a purely calorimetric setting. The question is at once suggested whether a corresponding identification of the internal energy of the body is possible by thermal tests alone.

This calls attention to a certain feature of incompleteness in the parallel as thus far drawn, in that the Carnot process implies the mediation of a working substance, while in the primitive form of the Black process only the two reservoirs are concerned, unless one considers the optical ether as mediator. It is, however, possible to imitate the net result of the irreversible conduction or radiation through the mediation of a gas, for instance, working in a cycle of the Carnot type except that such a part of the expansion on the upper isothermal is "free" that the net work of the cycle is zero. This illustrates that the primary condition for Black conservation during communication of the two reservoirs is of course not that there shall be no mediator but merely that the ultimate changes shall affect only those reservoirs; in contrast with the Carnot cycle, where some change in other bodies accompanies the non-vanishing work done. Accordingly, any case where it is possible to use a mediating body in such a way that this condition is satisfied, and such that the quantities of heat absorbed can be identified in terms of the changes in that body itself, can be thought of, not only as exhibiting conservation of thermal energy, but as leading also to a calorimetric identification of changes in what is to be called the internal energy of the body. The

simplest case is naturally that of a cycle passing through two states of the mediator, such as to connect those states in two different ways by a path consisting of an isothermal and an adiabatic, one path reversible, the other necessarily irreversible at least in part, and so adjusted that the net work of the cycle is zero. The experimental tests are then to be understood as verifying that the conditions of transitivity are satisfied, in fact with ratios identical with the b's above. In such a case the identification of the internal energy function is strictly analogous to that of the entropy by a Carnot cycle. That the identification of the two functions of state in this way can rightly be described as purely calorimetric is clear from the fact that, although the conditions involve full work in one case and no work in the other, still no quantitative comparison of heat and work is implied. Just how far the range of such cases extends it is not easy to say, but it may be guessed to be not far from coextensive with that in which a really experimental meaning attaches to the quantities of heat involved.

A more fundamental lack in the parallel appears when the further experimental facts are included which complete the classical first law, here more naturally called the last law. These show that in the case of the Carnot cycle the $q_1 - q_2$ is proportional to the work done, the factor of proportionality depending only on the units, or in other words that the conditions of transitivity are satisfied when mechanical energy is included with thermal energy; and more generally that work done is equivalent in any case to decrease in internal energy. The Carnot ratio then assumes the form of the ratio of efficiency; and, conversely, as Callendar has pointed out, the principle of efficiency combined with Carnot conservation leads to the principle of equivalence for reversible processes.

There is on the other hand, however, no physical quantity yet identified whose variations compensate those of the recognized thermal entropy. The discovery of such would be expected to make it possible to state certain conditions on irreversible processes in terms of an extended kind of Carnot conservation, instead of in terms of inequalities. It might also help to give physical meaning to the measure of probability, in terms of which entropy is expressed in statistical theories; perhaps utilizing some large scale coefficient related to the action constant of recent physical theory much as the gas constant is related to the agitation constant in the molecular theory. Many things suggest that if such a quantity exists, its setting may involve the relation of matter and radiation.

A certain "instinct for conservation" has sometimes been looked upon

as part of the natural equipment of the physical investigator, and the order of thought here sketched shows how fully successful in this subject is its guidance of the interpretation of experiment. With the exception of the single problematic instance mentioned—whose place so far as present knowledge goes is held by the inequalities that take such a unique place in physical theory—the basic features of thermodynamic phenomena are found in the four distinct types of transitivity listed, each admitting statement in terms of the language of conservation, which lead to the abstraction of the four corresponding fundamental notions: heat, thermal energy, entropy, thermo-mechanical energy. The corresponding arrangement suggested for the theory includes then five laws, four equations and one inequality. The experimental basis used is a blend of reversible and irreversible processes, and in particular the various experiments of Joule on equivalence deal mainly with irreversible processes of rather extreme type.

Since, however, mathematical developments in thermodynamics are so largely concerned with reversible processes it is natural to ask whether some basis could not be found for a theory of such processes by themselves, adequate for the complete theory so far as they are concerned. It will be shown in part II. that conservation of the first type only and Carnot's principle of efficiency, as formulated in terms of the empirical scale of heat, are together sufficient for such a basis.

Part II. The Scope of Carnot's Principle.

The actual course of development of thermodynamics has tended to obscure the real reach of both of Carnot's fundamental ideas. First, his conservation of caloric was rejected as erroneous instead of being recognized as distinct from that of Black and Joule; the irony of this appears when one notices that, for the processes he defines, a conservation essentially equivalent to his occurs as a theorem in the classical theory. Second, his principle of efficiency did not have its consequences developed independently, but rather it was merely superposed on the principle of equivalence, adding thus to the theory only the extra content it had to offer. From the very nature of his principle, however, in that it refers to a ratio of heat and work as related to two distinct temperatures, it would seem inevitable that it should lead to some kind of quantitative comparison of heat at different temperatures as well as of heat with work, independently of his postulate of conservation. In order to reveal the full scope of the principle therefore, and especially its independence of the ordinary principle of equivalence, it is natural to develop its consequences with only so much additional assumption

as is required to yield the general notion of a quantity of heat, abstracted from the properties of particular bodies.

Accordingly, for the alternative theory now to be presented, relating to reversible processes only, the basis of assumption is the Carnot postulate of efficiency, that for reversible cycles of his type the ratio of work done to heat absorbed on the upper isothermal is a universal function of the two temperatures; where quantities of heat are to be understood as known to be measurable in the sense of an empirical scale of heat as above described. Thus of the various types of conservation mentioned in part I. only the first or single-temperature type is now assumed, this being apparently the mildest basis on which Carnot's principle has intelligible meaning as one of possible common application to all kinds of bodies. As thus understood it will be shown to yield the entire thermodynamics of reversible processes. The existence of thermal energy and of entropy proves to be deducible without reference to the experimental basis of irreversible phenomena on which the theory of energy ordinarily rests. The conservation during reversible conduction, which is assumed, is the type where conservation of energy and of entropy are not distinct, so that only the generic notion "quantity of t-heat" is needed.

The case to be for convenience considered first is that of a fluid as working substance, its thermodynamic properties under the limited calorimetry defined being embodied in differential expressions

$$(1) \qquad dh = kdt + ldv, \qquad dw = pdv,$$

for heat absorbed and work done during a differential change under equilibrium pressure, where the coefficients k, l, p are for each particular body certain definite functions of v and t. Now merely as a mathematical proposition there exists for any system of this kind, with only two independent variables, an integrating divisor ω such that dh/ω is an exact differential ds; the ω is of course not uniquely determined, but any particular choice gives a function s determinate except for an additive constant. The s chosen is to serve simply as parameter of the adiabatic lines, whose differential equation is $dh = 0$, and later naturally appears as some function of the entropy, the canonical choice of s being the entropy itself.

The reasoning can be carried out in terms of the original variables (v, t), but for brevity it is convenient to transform to (s, t) as new independent variables. These are independent except when the latent heat of expansion l vanishes, in which case a true Carnot cycle is not possible since then an adiabatic is also an isothermal; this is a physically unreal

case which need not be pursued. It is also essentially general for the main purpose to suppose that the Jacobian $\partial(v, t)/\partial(s, t)$ is positive, so that the sense of equivalent cycles is the same in the (v, t) and (s, t) planes when the coördinates are taken in this order. Whatever the choice of the s, this transformation offers the convenience that a Carnot cycle is represented by a rectangle in the (s, t) plane. In terms of these new variables the heat and work take the forms

$$dh = \omega ds, \qquad dw = ads + bdt, \tag{2}$$

where ω, a, b are to be considered as functions of s and t; the explicit formulas connecting them with k, l, p are not needed. It will be clear also that the proof really applies to the general case of a two-variable system, since the same forms would result if the original expression for dw had a term in dt, and if the v and p were interpreted as any coördinate and corresponding generalized force.

If t_1 and t_2 be the higher and lower temperatures in the cycle Carnot's principle then imposes the condition

$$w/h_1 = H(t_1, t_2), \tag{3}$$

where H is the same function for all bodies when the same scales of heat and temperature are used for all. A change of the scale of heat, represented by putting $h = h'\rho(t)$ and thus giving $k' = k/\rho$, $l' = l/\rho$, is allowed for by putting

$$H'(t_1, t_2) = \rho(t_1)H(t_1, t_2).$$

This is still universal in the sense intended, so that if the principle is valid for one scale of heat it is valid for all.

The case in hand, for the cycle represented by the rectangle $(s = s_2 \cdots s_1,\ t = t_2 \cdots t_1)$ has

$$h_1 = \int_{s_2}^{s_1} \omega(s, t_1)ds, \qquad w = \int_{s_2}^{s_1}\int_{t_2}^{t_1} \varphi(s, t)dsdt, \tag{4}$$

in which

$$\varphi(s, t) = \frac{\partial a}{\partial t} - \frac{\partial b}{\partial s} = \frac{\partial(v, p)}{\partial(s, t)}, \tag{5}$$

where the area-integral for w is obtained by a known lemma from the initial perimeter integral. The fundamental condition is then that the relation

$$\int_{s_2}^{s_1}\int_{t_2}^{t_1} \varphi(s, t)dsdt = H(t_1, t_2)\int_{s_2}^{s_1} \omega(s, t_1)ds \tag{6}$$

must be an identity in (s_1, s_2, t_1, t_2).

Consideration of a range infinitesimal in t suggests the introduction of the function

$$\psi(t) = \left[-\frac{\partial H(t, t')}{\partial t'} \right]_{t'=t}, \tag{7}$$

which is the familiar Carnot function adapted to an arbitrary scale of heat as well as of temperature. For a cycle infinitesimal in s only

$$\int_{t_2}^{t_1} \varphi(s, t)dt = \omega(s, t_1)H(t_1, t_2), \tag{8}$$

whence

$$\varphi(s, t_2) = -\omega(s, t_1)\frac{\partial H(t_1, t_2)}{\partial t_2}, \tag{9}$$

the limiting form of which for range infinitesimal in t also is

$$\varphi(s, t_1) = \omega(s, t_1)\psi(t_1), \tag{10}$$

so that division shows the ratio $\varphi(s, t_1)/\varphi(s, t_2)$ to be a function of t_1, t_2 only, say for abbreviation $f(t_1, t_2)$, identically in s, t_1, t_2. Because of the symmetry of notation it is no longer necessary to keep the condition $t_1 > t_2$. If then t_0 be any particular value of t this result is equivalent to

$$\varphi(s, t) = \varphi(s, t_0)f(t, t_0),$$

so that φ is built of two factors, each a function of one of the variables only, which for later convenience may be written as derivatives:

$$\varphi(s, t) = \sigma'(s)\tau'(t), \tag{11}$$

where the factors can be understood as positive so that σ and τ are monotonic increasing functions. Then (10) gives

$$\omega(s, t) = \sigma'(s)\theta(t), \tag{12}$$

where by definition

$$\theta(t) = \tau'(t)/\psi(t). \tag{13}$$

The differential forms in (2) and the relation (5) become

$$dh = \sigma'(s)\theta(t)ds, \qquad dw = ads + bdt, \tag{14}$$

$$\frac{\partial a}{\partial t} - \frac{\partial b}{\partial s} = \sigma'(s)\tau'(t),$$

the last being equivalent to

$$\frac{\partial}{\partial t}(a - \sigma'\tau) = \frac{\partial b}{\partial s},$$

which indicates the existence of a function u such that

$$a = \sigma'(s)\tau(t) - \frac{\partial u}{\partial s}, \qquad b = -\frac{\partial u}{\partial t}, \tag{15}$$

which make

$$dw = \sigma'(s)\tau(t)ds - du = \frac{\tau(t)}{\theta(t)}dh - du. \tag{16}$$

This suggests the introduction of a particular scale of measurement of heat by the definition

$$dq = \frac{\tau(t)}{\theta(t)}dh, \tag{17}$$

so that

$$du = dq - dw, \qquad d\sigma = dh/\theta = dq/\tau, \tag{18}$$

where $d\sigma$, du are exact differentials, while dq in general would not be. In terms of the original differential forms (1) the result is then that there exist functions θ and τ of t only such that dh/θ and $\tau dh/\theta - dw$ are exact differentials. The dq and $d\sigma$ are the measures of heat on two special scales whose existence is implied in the Carnot principle.[1]

As to uniqueness, the mode of introduction of τ and θ shows that any two determinations for the same body or for different bodies are related by

$$\tau^* = \alpha\tau + \beta, \qquad \theta^* = \alpha\theta,$$

so that for the same dh:

$$dq^* = dq + \beta dh/\alpha\theta.$$

But since only the product $\sigma'\tau'$ is determined it is essentially general to hold α as unity, then the freedom left in the definition of dq can be used to arrange that equality in dh shall bring about equality in dq, by having $\beta = 0$; thus τ and θ may be understood as the same for all bodies.

In terms of the general and the two special scales of heat the efficiency ratio and the conditions of vanishing of the cyclic integrals of $d\sigma$ and du are

$$\frac{w}{h_1} = \frac{\tau_1 - \tau_2}{\theta_1}, \qquad \frac{w}{q_1} = \frac{\tau_1 - \tau_2}{\tau_1}, \qquad \frac{w}{\sigma_1} = \tau_1 - \tau_2;$$

$$\frac{h_1}{\theta_1} + \frac{h_2}{\theta_2} = 0, \qquad \frac{q_1}{\tau_1} + \frac{q_2}{\tau_2} = 0, \qquad \sigma_1 + \sigma_2 = 0;$$

$$w = \frac{h_1}{\theta_1/\tau_1} + \frac{h_2}{\theta_2/\tau_2} = q_1 + q_2 = \frac{\sigma_1}{1/\tau_1} + \frac{\sigma_2}{1/\tau_2};$$

[1] This proof should be compared with the deduction given by Larmor, *loc. cit.*, especially p. 332. He begins with the more primitive form of the Carnot postulate, that in order to have work done heat must fall in temperature, and considers also irreversible processes. The factorization which introduces one of his temperature functions results from a functional equation transcribing the coupling of two Carnot cycles. His $g(\theta)$ and $\psi(\theta)$ correspond to the $\theta(t)$ and $\tau(t)$ above; Raveau similarly deduces the existence of two distinct scales or functions of temperature. As to the use of the term "universal," however, the distinction should be noted, that the θ in the present paper, although the same for all bodies, depends on the scale of heat, while τ is independent of that scale. It is naturally the latter only that is to be considered truly universal as a scale of temperature.

inspection of which shows for one thing that θ depends on the scale of heat while τ does not. Thus τ/θ, $1/\theta$, and τ correspond to $B(t)$, $C(t)$, and $T(t)$ of Part I., while q and σ are thermal energy and entropy.

The parity of setting of the two special scales of heat is noticeable here as in Part I. It is hard to see how either can be said flatly to give the true measure of heat, though Callendar's view as to the preëminent claim of the entropy scale seems fully as reasonable as the common exclusive use of the energy scale. The latter has of course the obvious advantage for measurement and computation that it gives a constant ratio of work to thermal equivalent and approximate constancy of ordinary specific heats, but for theoretical purposes at least the entropy scale offers some advantages. For example, if for k/θ and l/θ be put κ and λ, these being then temperature-capacity for entropy and latent entropy of expansion, the differential forms with temperature on the τ-scale are

$$d\sigma = \kappa d\tau + \lambda dv, \qquad dw = pdv,$$

and the conditions are that $d\sigma$ and $\tau d\sigma - dw$ be exact differentials. These conditions are equivalent to the adapted Clapeyron and Clausius equations

$$\lambda = \frac{\partial p}{\partial \tau}, \qquad \frac{\partial \kappa}{\partial v} = \frac{\partial^2 p}{\partial \tau^2},$$

which are so simply interpretable on the graph of the isochoric (p, τ) curve.

To extend the theory to a system with more than two coördinates it is convenient to use the τ-scale of temperature and the σ-scale of heat, as determined for two-variable systems. A system with n coördinates of configuration, say $v_1 \cdots v_n$, will then be characterized by the differential forms

$$d\sigma = \kappa d\tau + \Sigma \lambda_i dv_i, \qquad dw = \Sigma p_i dv_i.$$

The Carnot principle may then be understood to be applicable to every two-variable process which such a system can undergo, through the presence of possible or conceivable constraints. This is equivalent to the condition that if for $v_1 \cdots v_n$ be put any arbitrary functions of τ and a single other parameter v, then $d\sigma$ and $\tau d\sigma - dw$ must be exact differentials in these two variables. The conditions for this prove to be equivalent to those under which the same expressions are exact differentials in the $n + 1$ variables, regarded as independent. To show this it is enough to consider only the following types of cycle: (a) where only one of the variables v_i varies, (b) where only two are affected, these undergoing variations proportionate but in arbitrary ratio. With such cycles,

starting at an arbitrary state of the system, the Carnot principle yields, from (*a*) the Clapeyron and Clausius equations for each of the variables separately, and from (*b*) the additional conditions

$$\frac{\partial p_i}{\partial v_j} = \frac{\partial p_j}{\partial v_i}, \qquad \frac{\partial \lambda_i}{\partial v_j} = \frac{\partial \lambda_j}{\partial v_i},$$

which indicate the conservation in an isothermal cycle of work and of heat separately. The scales θ and τ and the equations in (17) and (18) thus apply to these more general systems.

If for such a system the heat scale be still left arbitrary, the result is that dh/θ and $\tau dh/\theta - dw$ are exact differentials of functions of state σ and u, so that $dh = \theta d\sigma$, $dw = \tau d\sigma - du$. Now while a system with two variables only can have but two independent functions of state, one with more types of variation can have a corresponding number. But not more than two independent functions can have differentials linearly expressible in terms of the same two fundamental differential forms; in fact, in the case here, any function of state whose differential is a linear combination of dh and dw must be a function of σ and u. In this sense the theory of energy and entropy, and therefore the Carnot principle, yields the entire theory that can be based solely on dh and dw.

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THE SIZE AND SHAPE OF THE ELECTRON.[1]

BY ARTHUR H. COMPTON.

SYNOPSIS.—Attention is called to two outstanding differences between experiment and the theory of scattering of high frequency radiation based upon the hypothesis of a sensibly point charge electron. In the first place, according to this theory the mass scattering coefficient should never fall below about .2, whereas the observed scattering coefficient for very hard X-rays and γ-rays falls as low as one fourth of this value. In the second place, if the electron is small compared with the wave-length of the incident rays, when a beam of γ-rays is passed through a thin plate of matter the intensity of the scattered rays on the two sides of the plate should be the same, whereas it is well known that the scattered radiation on the emergent side of the plate is more intense than that on the incident side.

It is pointed out that the hypothesis that the electron has a diameter comparable with the wave-length of the hard γ-rays will account qualitatively for these differences, in virtue of the phase difference between rays scattered by different parts of the electron. The scattering coefficient for different wave-lengths is calculated on the basis of three types of electron: (1) A rigid spherical shell of electricity, incapable of rotation; (2) a flexible spherical shell of electricity; (3) a thin flexible ring of electricity. All three types are found to account satisfactorily for the meager available data on the magnitude of the scattering coefficient for various wave-lengths. The rigid spherical electron is incapable of accounting for the difference between the emergent and the incident scattered radiation, while the flexible ring electron accounts more accurately for this difference than does the flexible spherical shell electron.

It is concluded that the diameter of the electron is comparable in magnitude with the wave-length of the shortest γ-rays. Using the best available values for the wave-length and the scattering by matter of hard X-rays and γ-rays, the radius of the electron is estimated as about 2×10^{-10} cm. Evidence is also found that the radius of the electron is the same in the different elements. In order to explain the fact that the incident scattered radiation is less intense than the emergent radiation, the electron must be subject to rotations as well as translations.

I. THE SCATTERING OF HIGH FREQUENCY RADIATION.

THE radius of the electron is usually calculated from its kinetic energy when in motion, taking this to be identical with its magnetic energy. According to the customary assumption that the charge on an electron is uniformly distributed over the surface of a sphere, the radius of the sphere as thus calculated is about 1×10^{-13} cm. There are, however, a number of phenomena in connection with the scattering and absorption of high frequency radiation by matter, which appear to be

[1] A preliminary paper on this subject was read before the American Physical Society, December 28, 1917 (PHYS. REV., 11, 330, 1918). Cf. also J. Wash. Ac. Sci., 8, 1, 1918.

inexplicable according to classical electrodynamics if the dimensions of the electron are taken to be of this order of magnitude, whose explanation is obvious if the electron is assumed to be a flexible ring of electricity whose radius is comparable with the wave-length of short γ-rays. This paper is the first of a series of three, which will deal respectively with the scattering of high-frequency radiation, the absorption of high-frequency radiation, and the nature of the ultimate magnetic particle. The present discussion will deal with certain outstanding differences between experiment and the theory of scattering of high frequency radiation based upon the hypothesis of a sensibly point charge electron, and it will be shown that these differences may be explained on the basis of an electron of relatively large size. In order to preserve the directness of the argument, the details of the calculations will be reserved for the latter part of the paper.

PART I.

A. *The Scattering Coefficient of High Frequency Radiation.*

On the hypothesis that the electron is sensibly a point charge of electricity, Sir J. J. Thomson has shown[1] that the ratio of the energy of the electromagnetic radiation scattered by an isolated electron to the energy incident upon it is given by the expression

$$\frac{8\pi}{3}\frac{e^4}{m^2C^4}.$$

Here e and m are respectively the charge and mass of the electron, and C is the velocity of light. If the electrons in any substance act independently of each other, the scattering coefficient per unit mass of the substance will therefore be

$$\frac{\sigma}{\rho} = \frac{8\pi}{3}\frac{Ne^4}{m^2C^4}, \tag{1}$$

where σ is the ratio of the scattered to the incident energy per unit volume of the material, ρ is its density, and N is the number of electrons in unit mass of the substance.

Since this scattered energy is lost from the primary beam, the quantity σ/ρ represents also the part of the mass absorption coefficient which is due to scattering. As Barkla has pointed out,[2] there may be absorption due to other causes, such as the production of secondary beta or cathode rays, but this absorption due to scattering must always be present. Moreover, if the electrons in the absorbing material are grouped together in regions which are small compared with the wave-length of the incident

[1] J. J. Thomson, Conduction of Electricity through Gases, 2d ed., p. 325.

[2] C. G. Barkla and M. P. White, Phil. Mag., 34, 275, 1917.

beam, the electrons do not scatter independently. The rays scattered by the electrons in this case overlap in such a manner that a certain amount of "excess scattering" occurs. There is, however, no arrangement of the electrons which will result in less scattering than when they act independently. On the hypothesis of a point charge electron, it is possible for the scattering, and hence for the mass absorption coefficient, to be smaller than that predicted by Thomson's expression (1) only in case the electrons are held in position so firmly that their natural period of vibration is shorter than the period of the incident radiation.

In making the calculations from Thomson's theory, it may be assumed that the number of electrons in an atom which are effective in scattering the incident radiation is equal to the atomic number. This assumption is supported in the case of the lighter elements by the experiments of Barkla and Dunlop[1] when X-rays of ordinary hardness are used. It would seem possible that with the higher frequency γ-rays certain electrons might be effective in scattering which are too rigidly bound to scatter X-rays. Such an effect, however, would mean an increase rather than a decrease in the scattering for the shorter wave-lengths. That the atomic number is the number of effective electrons when γ-rays are used, is confirmed by the observations of Soddy and Russell[2] and of Ishino[3] to the effect that for the shortest rays the amount of energy scattered by atoms of the different elements is accurately proportional to their atomic numbers. This means that all the electrons outside of the nucleus are effective in producing absorption when hard γ-rays are used. If the electron is sensibly a point charge of electricity, the scattered energy should therefore be at least as great as the value assigned by equation (1).

Barkla and Dunlop[4] have shown that for a considerable range of wave-lengths of X-rays the mass scattering coefficients of the lighter elements are given accurately by equation (1) if the number of electrons in the atom is taken to be approximately half the atomic weight. For elements of high atomic weight, the scattering becomes greater than this value except for very short wave-lengths, indicating that the electrons are so closely packed that "excess scattering" occurs. For wave-lengths less than 2×10^{-9} cm., however, Barkla and White[5] have shown that the total mass absorption coefficient of the light elements is less than the value theoretically calculated for the mass scattering coefficient alone; and Soddy and Russell[6] have found that for the hard γ-rays from Radium

[1] C. G. Barkla and J. G. Dunlop, Phil. Mag., 31, 222, 1916.

[2] Soddy and Russell, Phil. Mag. 18, 620, 1910; 19, 725, 1910.

[3] M. Ishino, Phil. Mag., 33, 140, 1917.

[4] C. G. Barkla and J. G. Dunlop, *loc. cit.*

[5] C. G. Barkla and M. P. White, *loc. cit.*, p. 277.

[6] Soddy and Russell, *loc. cit.*

C the absorption of substances of lower atomic weight than mercury is only a small fraction of that required by Thomson's expression. Direct measurements of the scattering of hard γ-rays confirm the conclusions based on absorption measurements. Thus it has been found[1] in the case of radiation of very high frequency that the mass scattering coefficient falls as low as one fourth of the value predicted by Thomson's theory.

As has just been pointed out, it is impossible, according to classical electrodynamics, to account for this low scattering and absorption of radiation of very high frequency by matter if the electron is taken to be sensibly a point charge of electricity. If, on the other hand, the electron is considered to have a radius comparable with the wave-length of the incident radiation, a qualitative explanation of the phenomenon of low scattering for short wave-lengths is obvious. The effect of this hypothesis is to make an appreciable phase difference between the rays scattered by different parts of the electron. Thus the radiation scattered from A, Fig. 1, traverses a longer path between S and P than does the ray scattered from the part of the electron at B. If the wave-length is many times the diameter of the electron, the phase difference between these two rays will be negligible, and the reduction in the intensity of the scattered beam will be inappreciable; if, however, the difference in the two paths is comparable with the wave-length of the incident radiation, the phase difference will be such that the intensity of the ray scattered to P will be much reduced. The assumption of a relatively large electron is therefore capable of explaining qualitatively the observed decrease in the scattering of electromagnetic radiation when the wave-length becomes very short.

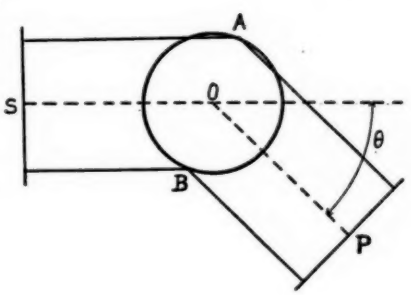

Fig. 1.

Calculation of the Scattering. I. *Rigid Spherical Electron.*—The exact manner in which the scattering will decrease with shorter wave-lengths will of course depend upon the form of electron considered. For example, taking the simplest case of the scattering due to a rigid, uniform, spherical shell of electricity, incapable of rotation, we find

$$\frac{\sigma}{\rho} = \frac{8\pi}{3}\,\frac{e^4N}{m^2C^4}\sin^4\left(\frac{2\pi a}{\lambda}\right)\Big/\left(\frac{2\pi a}{\lambda}\right)^4, \tag{2}$$

[1] M. Ishino, *loc. cit.*

where a is the radius of the spherical shell and λ is the wave-length of the incident beam. The details of the derivation of this expression will be found in Part 2, Section 1. If $a = 10^{-13}$ cm., as usually assumed, this is practically identical with equation (1), even for radiation of the shortest known wave-length. The relative values of the scattering according to this expression are shown in curve *I*, Fig. 2, for different values of λ/a. In this diagram the value $\sigma/\sigma_0 = 1$ indicates the magnitude of the mass scattering if the electron were sensibly a point charge of electricity, and the calculated values are given in terms of this quantity.

2. *Flexible Spherical Electron.*—It would appear more reasonable to suppose that the spherical shell electron is subject to rotational as well as to translational displacements when traversed by a γ-ray. The scattering due to such an electron is difficult to calculate, but an approximate expression can be obtained if the electron is considered to be perfectly flexible, so that each part of it can be moved independently of the other parts. On this hypothesis it can be shown (cf. Part 2, Section 2) that the intensity of the beam scattered by an electron at an angle θ with an unpolarized beam of γ-rays is given by the expression,

$$(1) \qquad I_\theta = I\frac{e^4(1+\cos^2\theta)}{2L^2m^2C^4}\left\{\sin^2\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)\Big/\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)^2\right\}.$$

Here I is the intensity of the incident beam, L is the distance at which the intensity of the scattered beam is measured, and the other quantities have the same meaning as before. The mass absorption coefficient due to the scattering by such an electron is therefore,

$$(4) \qquad \frac{\sigma}{\rho} = 2\pi NL^2\int_0^\pi \frac{I_0}{I}\sin\theta d\theta.$$

This integral may be evaluated graphically or by expansion into a series (*cf. infra*, equation 17). The values of σ/σ_0 according to equation (4) are plotted in curve *II*, Fig. 2. The values for a rigid spherical electron which is subject to rotation should lie between curves *I* and *II* for the range of wave-lengths for which curve *II* is plotted.

3. *Ring Electron.*—According to electromagnetic theory it is obvious that the mass of an electron cannot be accounted for on the basis of a uniform distribution of electricity over the surface of a sphere of radius comparable with the wave-length of γ-rays. Much the same effect, so far as the scattering of high frequency radiation is concerned, results from the conception of the electron as a ring of electricity of relatively large diameter, similar in form to the "magneton" suggested by A. L. Parson.[1] It has been shown by Webster[2] and Davisson[3] that the assump-

[1] A. L. Parson, Smithsonian Misc. Collections, Nov., 1915.

[2] D. L. Webster, PHYS. REV., 9, 484, 1917.

[3] Davisson, PHYS. REV., 9, 570, 1917.

tion of such an electron is compatible with the electromagnetic theory of mass.

The exact calculation of the scattering produced by a thin ring of electricity is difficult. A chief factor in the complexity of the problem is the fact that the effective electromagnetic mass of a short arc of the ring differs according as it is accelerated parallel to the tangent to the arc, parallel to the axis of the ring, or parallel to a radius of the ring. The ratios of the effective masses along these three axes depends moreover upon the speed with which the electricity in the ring is rotating. In order to make the problem manageable, the assumptions have been made that the mass of an arc element is the same in all directions, and that the velocity of the electricity in the ring is small compared with the velocity of light. On the basis of these assumptions the mass scattering coefficient for a flexible electronic ring is found to be

$$(5) \qquad \frac{\sigma}{\rho} = \frac{8\pi}{3}\frac{Ne^4}{m^2C^4}\left\{1 - a\left(\frac{a}{\lambda}\right)^2 + b\left(\frac{a}{\lambda}\right)^4 - c\left(\frac{a}{\lambda}\right)^6 + \cdots\right\},$$

where the coefficients $a, b, c, \cdots$ are constants which are evaluated below (cf. equation 21). The relative values of the scattering according to this expression are shown in curve *III*, Fig. 2. The scattering of γ-rays

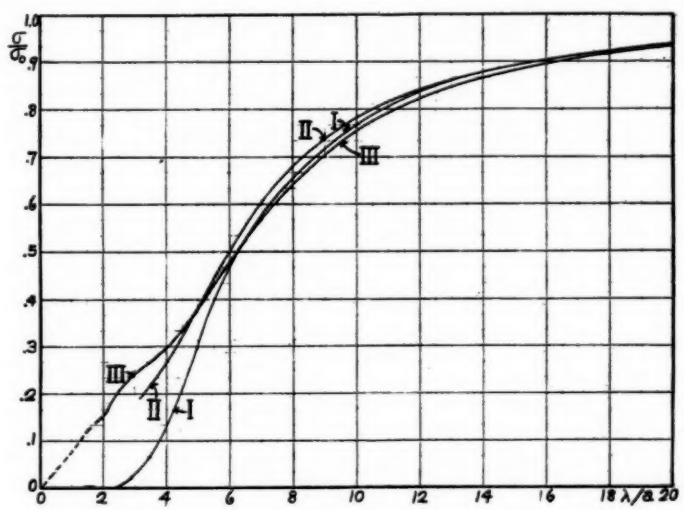

Fig. 2.

by a ring electron as thus calculated is an approximation which will doubtless correspond closely with the true value for relatively long waves, but which may differ appreciably for the shortest known radiation.

Unfortunately the experimental data are too meager to submit these formulæ to accurate quantitative test. There are, however, three points

on the curve which have been established with some care. Barkla and Dunlop[1] have found that for relatively soft X-rays the light elements scatter according to equation (1), so that the part of the curves where λ/a is large is verified. Hull and Rice[2] have estimated from their absorption measurements that for X-rays and γ-rays whose wave-lengths are in the neighborhood of 0.15×10^{-8} cm. the value of σ/ρ for aluminium is 0.12. Taking the number of electrons in an aluminium atom to be 13, this gives for the relative scattering, 0.64. According to curve *I* this corresponds to an electronic radius of 1.9×10^{-10} cm. Curve *II* gives 2.0×10^{-10} cm., and curve *III*, 1.9×10^{-10} cm.[3] Ishino[4] finds that the value of σ/ρ for aluminium, using the hard γ-rays from radium C, is about 0.045, which means a value for the relative scattering of 0.24. The work of Rutherford and Andrade[5] shows that the principal part of the "homogeneous" radiations from radium C consists of a strong line $\lambda = 0.099$, and a weaker line $\lambda = .071$, $\times 10^{-8}$ cm. Both of these lines were prominent in Ishino's experiment, in which he filtered the γ-rays through a centimeter of lead. Rutherford has pointed out,[6] however, from a consideration of the velocities of the β-particles, that there must be a certain amount of radiation of much shorter wave-length. The existence of such extremely hard rays is confirmed by the fact that the absorption coefficient of the penetrating radiation of the atmosphere as determined at high altitudes is much smaller than that of the hard γ-rays from radium C, such as used by Ishino. The fact that it is impossible to detect these very short waves by crystal analysis, however, indicates that their effectiveness in the scattered beam is small compared with that of the two lines observed by Rutherford and Andrade. It seems reasonable, therefore, to take for the effective wave-length of the γ-rays used in Ishino's scattering experiments about $.08 \times 10^{-8}$ cm.[7] This gives for the value of the electronic radius, from curve *I*, 1.7, from curve *II*, 2.1 and from curve *III*, 2.7, $\times 10^{-10}$ cm.

[1] C. G. Barkla and Dunlop, *loc. cit.*

[2] A. W. Hull and M. Rice, PHYS. REV., 8, 326, 1916.

[3] In the second part of this paper, by using a more accurate formula for the mass absorption coefficient, the data of Hull and Rice will be shown to lead to a value of $(1.85 \pm .04) \times 10^{-12}$ cm., if the electron is taken to be a ring.

[4] M. Ishino, *loc. cit.*, p. 141.

[5] Sir E. Rutherford and Andrade, Phil. Mag., 28, 263, 1916.

[6] Sir E. Rutherford, Phil. Mag., 34, 153, 1917.

[7] In the paper last referred to, Rutherford estimated the effective wave-length of Ishino's γ-rays to be much shorter than the value here used. His estimate is based upon measurements of the absorption of high frequency X-rays filtered by means of a lead filter. He calculated the frequency of the X-rays according to the relation $h\nu = eV$, taking V to be the maximum voltage applied to the tube. As is apparent from the work of Rutherford, Barnes and Richardson (Phil. Mag., 30, 339, 1915), this relation does not express the *effective* fre-

The value of σ/ρ given by Hull and Rice is a mean over a relatively large range of wave-lengths, and Barkla is of the opinion[1] that Ishino's value of the scattering of the γ-rays from radium *C* is appreciably in in error because of a too high estimate of the true absorption. Thus, though the experimental values of the electronic radius agree best on the basis of the flexible spherical shell electron, as represented in curve *II*, the accuracy of the experiments is by no means sufficient to distinguish between the three hypotheses.

The important thing to notice is that if the electrons had dimensions comparable with 10^{-13} cm., as usually assumed, the scattering should be represented by the upper line of Fig. 2 where $\sigma/\sigma_0 = 1.0$. The fact that experiment gives consistently lower values when short wave-lengths are used is sufficient proof that the electron is not sensibly a point charge of electricity. On the other hand, it is possible to account for this reduced scattering within the probable experimental error if the electron has a radius of 2×10^{-10} cm.

B. The Dissymmetry of the Scattering of Hard γ-rays on the Incident and Emergent Sides of a Plate.

A second difficulty which is found with Sir J. J. Thomson's simple theory is that it predicts that if a beam of X-rays is passed through a thin plate of matter, the intensity of the scattered rays on the two sides of the plate should be the same. Barkla and Ayers[2] have shown that, for rather hard X-rays and for those substances of low atomic weight whose mass scattering coefficients can be calculated accurately by equation (1), this second prediction of Thomson's theory is also valid. On the other hand, it is well known that both in the case of relatively soft X-rays and in the case of hard γ-rays the scattered radiation on the emergent side of the plate is more intense than that on the incident side.

When heavy atoms and long waves are used, the dissymmetry between the emergent and the incident scattered radiation is accompanied by an increase in the total scattered energy. For this reason the phenomenon is described by the term "excess scattering." It is satisfactorily accounted for[3] by the fact that the electrons in the heavy atoms do not act independently in scattering the longer wave-length X-rays, since

quency of the filtered rays, especially when a lead filter is used. This doubtless accounts for the fact, which will be brought out in the following paper, that Rutherford's determinations of the absorption do not agree with those of Hull and Rice, who measured the absorption coefficient of homogeneous X-rays of known wave-length.

[1] C. G. Barkla and M. P. White, *loc. cit.*, p. 278.

[2] Barkla and Ayers, Phil. Mag., 21, 271, 1911.

[3] C. G. Darwin, Phil. Mag., 27, 329, 1914; D. L. Webster, Phil. Mag., 25, 234, 1913.

they are grouped so closely together that the rays scattered by the different electrons are in nearly the same phase. This has the effect of increasing the total scattering. But also, since the phase difference between the rays from the different electrons in an atom is less for the scattered rays which make small angles with the primary beam, there is greater reinforcement and hence greater intensity on the emergent than on the incident side of the scattering atom.

This explanation cannot be applied, however, to the case of the unsymmetrical scattering of very hard rays. This is clear for two reasons. In the first place, if an atom of medium weight is traversed by rays of increasing hardness, at first excess scattering occurs as described above; but as the wave-length becomes shorter the scattered radiation becomes nearly symmetrical until the scattered energy can be calculated according to Thomson's formula (1). The electrons now, therefore, are scattering independently, and must continue to do so for all shorter wave-lengths. Thus we see that the dissymmetry in the scattering which reappears as the wave-length becomes very short cannot be accounted for by the mutual action of the separate electrons. In the second place, the phenomenon of unsymmetrical scattering for very short waves is distinguished from the excess scattering which occurs with longer waves by the fact that in the former case the dissymmetry is accompanied not by an increase but by a decrease in the total scattering. If the phenomenon were due to the mutual action of the electrons, it would be accompanied by an increased total scattering, as before. It is thus evident that the unsymmetrical scattering of very short electromagnetic waves is due not to groups of electrons in the atoms, but to some property of the individual electrons.

The qualitative explanation of this phenomenon on the basis of our large electron hypothesis is at once apparent. Referring again to Fig. 1, it is obvious that if the diameter of the electron is comparable with the wave-length of the radiation, there will be an appreciable difference in phase between the rays scattered from different parts of the electron. Since this phase difference is greater for rays scattered at large than for those at small angles, the intensity of the incident radiation will be in the former case the more strongly reduced. In order to explain this phenomenon it is not sufficient, however, merely to assume that the electron is relatively large. For example, the hypothesis of the electron as a rigid spherical shell, incapable of rotation, though resulting in a reduced total scattering, would give rise to symmetrical scattering on the incident and emergent sides of a plate. To account for the observed dissymmetry, the further assumption must be made that the incident

electromagnetic wave is capable of moving the different parts of the electron relatively to each other.

If the electron is sensibly a point charge of electricity, the intensity of the beam scattered by an electron at an angle θ with the incident beam is[1]

$$I_\theta = I\frac{e^4(1+\cos^2\theta)}{2L^2m^2C^4}. \tag{6}$$

The corresponding expression for an electron in the form of a flexible spherical shell of electricity has already been given:

$$I_\theta = I\frac{e^4(1+\cos^2\theta)}{2L^2m^2C^4}\left\{\sin^2\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)^2\Big/\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)^2\right\}. \tag{3}$$

For the ring type electron we obtain

$$I_\theta = I\frac{e^4(1+\cos^2\theta)}{2L^2m^2C^4}\left\{1-\alpha\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)^2+\beta\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)^4-\cdots\right\}, \tag{7}$$

where the values of the constants α, β, γ, etc., are those determined below (equation 20). When a/λ remains small, the scattering according to both expressions (3) and (7) approaches the value for a point charge electron (6).

D. C. H. Florance[2] has determined experimentally the values of the relative intensity of the radiation scattered at different angles when the hard γ-rays from radium bromide traverse a plate of iron. His values are indicated in Fig. 3 by circles. Taking the effective wave-length of these rays to be $.09 \times 10^{-8}$ cm., and using in equations (3) and (7) $a = 2 \times 10^{-10}$ cm. as above estimated, the relative scattering at different angles may be calculated. The intensity of the radiation scattered at different angles by a point charge electron is indicated in Fig. 3 by the outer solid curve, that due to the spherical shell electron by the inner solid curve, and that from the ring form electron by the broken curve. Inasmuch as the γ-rays used by Florance were heterogenous, and as the softer rays are scattered relatively more strongly at larger angles, the agreement of the experimental values with either of the inner curves is as good as can be expected. The important point to be noticed is, however, that the experimental values are entirely out of harmony with

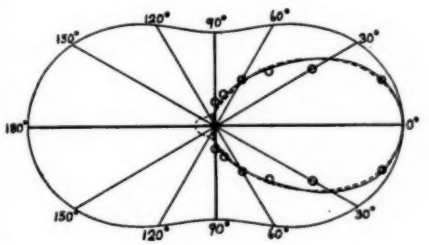

Fig. 3.

[1] J. J. Thomson, Conduction of Electricity through Gases, 2d ed., p. 326.

[2] D. C. H. Florance, Phil. Mag., 20, 921, 1910.

what is to be expected if the electron is sensibly a point charge of electricity.

A better quantitative test of this explanation of the dissymmetry of scattered γ-radiation is afforded by determinations of the ratio of the total radiation scattered on the incident side of a plate struck by hard γ-rays to that scattered on the emergent side. The theoretical value of this ratio is

$$\frac{I_i}{I_e} = \int_{\pi/2}^{\pi} I_\theta \sin\theta d\theta \Big/ \int_0^{\pi/2} I_\theta \sin\theta d\theta. \tag{8}$$

The curves of Fig. 4 give the values of this ratio for different values of λ/a, the broken curve being calculated on the basis of the spherical

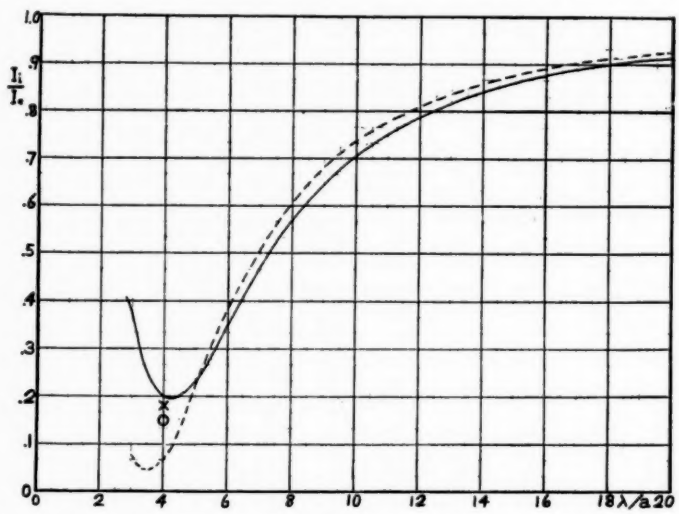

Fig. 4.

electron. These curves doubtless explain at least in part the observation of Florance[1] that the "incident" scattered rays are softer than the "emergent" and the primary rays, since they show that the relative amount of rays scattered backward is much greater for soft or long wave-length γ-rays than for the harder radiation.

The ratio of the incident to the emergent radiation has been determined for the hard γ-rays from radium C by Madsen,[2] who found the value 18 per cent., and Ishino,[3] who found 15 per cent. Assuming for the effective wave-length in this case $\lambda = 0.08 \times 10^{-8}$ cm., and for the radius of the electron 2×10^{-10} cm., as estimated above, Ishino's datum

[1] D. C. H. Florance, Phil. Mag., 27, 225, 1914.

[2] Madsen, Phil. Mag., 17, 423, 1909.

[3] M. Ishino, *loc. cit.*, p. 138.

for this ratio is represented by the open circle in Fig. 4 and Madsen's datum by the cross. It is possible that neither of the theoretical values agree within the probable experimental error with these determinations, but in view of the approximate method of calculating the scattering by a ring electron the difference is not serious. The fact that the predicted values are of the proper order of magnitude is strong evidence that the dissymmetry in the scattering of γ-rays by matter is due to the interference of the rays scattered by different parts of the electron. Thus not only must the electron have a size comparable with the wave-length of γ-rays, but it must also be subject to rotations or be sufficiently flexible for γ-rays to move its different parts relatively to each other.

C. *Conclusions.*

As has been pointed out, therefore, according to classical electrodynamics the mass scattering coefficient for X-rays and γ-rays passing through matter should never fall below the value 0.18, as calculated on the basis of Thomson's theory, if an electron of the usual dimensions is postulated. Experiment shows, however, that for very high frequency radiation the scattering is much less than this. It is possible that certain assumptions regarding the conditions for scattering radiant energy, contrary to classical theory, might be made which would account for the observed low value of the scattering for very high frequencies. As long as the idea of the point charge electron is retained, however, no such assumptions can account for the observed dissymmetry between the incident and the emergent scattered radiations. Unless the theory that X-rays and γ-rays consist of waves or pulses is abandoned, the only possible explanation of this dissymmetry would seem to be that the scattering particles have dimensions comparable with the wave-length of the rays which they scatter. Since the scattering particles have been shown to be the electrons, the statement may therefore be made with confidence that *the diameter of the electron is comparable in magnitude with the wave-length of the shortest γ-rays.*

According to the best available values for the wave-length and the scattering by matter of hard X-rays and γ-rays, *the radius of the electron is about* 2×10^{-10} *cm.*

The fact that the scattering of hard γ-rays by atoms of the different elements is proportional to the atomic number shows that if the number of the electrons in an atom which are effective in scattering is equal to the atomic number, *the radius of the electron is the same in the different atoms.* This is clear, since if the electron had smaller dimensions in the atoms of one element, the scattering coefficient of this element would

not decrease as rapidly for shorter wave-lengths, and the scattering by the different atoms would not be proportional to the number of electrons in the atoms.

In order to explain the fact that the emergent scattered radiation is more intense than the incident radiation, it is necessary to assume further that the different parts of the charge of the electron can possess certain motions independently of each other. That is, *the electron is subject to rotations as well as translations.*

PART 2.

1. *To calculate the energy scattered by a rigid spherical shell electron, incapable of rotation, whose diameter is comparable in magnitude with the wave-length of the incident radiation.*

Let us first derive an expression for the acceleration to which such an electron is subject when traversed by an electromagnetic wave, and then determine the energy scattered by integrating the intensity of the beam due to this acceleration over the surface of a sphere drawn with the electron at the center.

In Fig. 5, let us suppose that the γ-ray traverses the electron along the axis Z. We shall let A represent the amplitude of the incident wave, X its electric intensity at the plane z, and λ its wave-length. The radius of the electron we shall call a, and η will represent the charge on the surface of the electron between two planes z_1 and z_2 placed unit distance apart. As the electricity is by hypothesis distributed uniformly over the surface of the sphere, η is constant between $z = -a$ and $z = +a$, and the total charge on the electron is $e = 2a\eta$. The electric intensity at the plane z at any instant may be expressed by the relation,

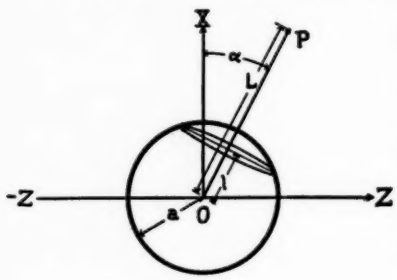

Fig. 5.

$$X = A \cos 2\pi \left(\frac{\delta - z}{\lambda} \right),$$

where $2\pi\delta/\lambda$ is the phase angle at $z = 0$ at that instant. The total force acting on the electron at this instant is therefore,

$$F = \int_{-a}^{a} A \cos 2\pi \left(\frac{\delta - z}{\lambda} \right) \eta dz$$

$$= \frac{A\eta\lambda}{\pi} \cos 2\pi \frac{\delta}{\lambda} \sin 2\pi \frac{a}{\lambda},$$

and the acceleration of the electron is

$$\ddot{x} = \frac{A\eta\lambda}{\pi m}\cos\frac{2\pi\delta}{\lambda}\sin\frac{2\pi a}{\lambda}. \tag{9}$$

Let us now calculate the intensity of the scattered ray at a distance L along the line OP which makes an angle α with the direction OX of the acceleration. According to classical theory the electric intensity at P due to a point charge electron at O subject to this acceleration would be

$$\frac{e\ddot{x}\sin\alpha}{LC^2} \tag{10}$$

where C is the velocity of light. Replacing e by ηdl and $\ddot{x}$ by its value as defined above, and integrating over the electron along the axis L from $l = -a$ to $l = +a$, the electric intensity of the scattered beam at L, α becomes:

$$\begin{aligned} R_{L,\alpha} &= \frac{\sin\alpha}{LC^2}\int_{-a}^{a}\frac{A\eta\lambda}{\pi m}\sin 2\pi\frac{a}{\lambda}\cos\frac{2\pi}{\lambda}(\delta - L + l)\eta dl \\ &= \frac{\eta^2\lambda A}{\pi mLC^2}\sin\alpha\sin 2\pi\frac{a}{\lambda}\int_{-a}^{a}\cos\frac{2\pi}{\lambda}(\delta - L + l)dl \\ &= \frac{\eta^2\lambda^2 A}{\pi^2 LmC^2}\sin^2 2\pi\frac{a}{\lambda}\sin\alpha\cos 2\pi\frac{\delta - L}{\lambda}. \end{aligned}$$

The amplitude of the electric vector of the scattered wave at the point L, α is therefore

$$A_{L,\alpha} = \frac{\eta^2\lambda^2 A}{\pi^2 LmC^2}\sin^2 2\pi\frac{a}{\lambda}\sin\alpha,$$

or substituting for η its value $e/2a$,

$$A_{L,\alpha} = \frac{Ae^2}{LmC^2}\frac{\sin^2(2\pi a/\lambda)}{(2\pi a/\lambda)^2}\cdot\sin\alpha.$$

The intensity of the radiation at this point is

$$I_{L,\alpha} = cA_{L,\alpha}^2 = \frac{cA^2e^4}{L^2m^2C^4}\frac{\sin^4(2\pi a/\lambda)}{(2\pi a/\lambda)^4}\sin^2\alpha,$$

so that the total energy scattered by the electron is

$$\begin{aligned} E_s &= \int_0^{\pi} I_{L,\alpha}\cdot 2\pi L\sin\alpha\cdot L d\alpha \\ &= \frac{2\pi cA^2e^4}{m^2C^4}\cdot\frac{\sin^4(2\pi a/\lambda)}{(2\pi a/\lambda)^4}\int_0^{\pi}\sin^3\alpha d\alpha \\ &= \frac{8\pi cA^2e^4}{3m^2C^4}\cdot\frac{\sin^4(2\pi a/\lambda)}{(2\pi a/\lambda)^4}. \end{aligned}$$

The energy incident on unit area at the electron is, however, $I = cA^2$, so that the fraction of the incident energy scattered by the electron is

$$E_s/I = \frac{8\pi e^4}{3m^2C^4} \frac{\sin^4 (2\pi a/\lambda)}{(2\pi a/\lambda)^4}. \tag{11}$$

When a is small compared with λ this becomes

$$\frac{e^4}{m^2C^4}, \tag{12}$$

which is identical with the value given by Thomson[1] for a sensibly point charge electron.

If there are N electrons per unit mass of any substance, the mass scattering coefficient of the substance is therefore

$$\frac{\sigma}{\rho} = \frac{8\pi}{3} \frac{e^4N}{m^2C^4} \frac{\sin^4 (2\pi a/\lambda)}{(2\pi a/\lambda)^4}, \tag{13}$$

where σ is the scattering coefficient per unit volume and ρ is the density of the scattering material.

2. *To calculate the energy scattered by an electron in the form of a flexible spherical shell of electricity.*

We shall treat this problem as if the mass of an element of the spherical shell were independent of the rest of the electron, being equal to $dm = m \cdot ds/s$, where s is the area of the surface of the electron, and m is its mass. As has been pointed out in part I. of this paper, the electro-magnetic mass of a spherical electron of the size here considered would be negligible. This form of electron is therefore only a convenient hypothesis to use in calculating the general effect on the scattering to be expected with any form of electron when the wave-length of the incident radiation approaches its largest dimensions.

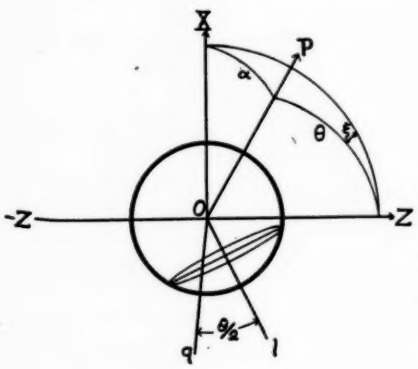

Fig. 6.

Let us suppose that the γ-ray strikes the electron when moving in the direction $-ZOZ$, and determine the intensity of the beam scattered in the direction OP. As shown in Fig. 6, OP makes the angle θ with the incident ray, and the angle α with the direction OX of the electric vector of the incident ray. The plane POZ is inclined at the dihedral angle ξ

[1] J. J. Thomson, *loc. cit.*

with the plane XOZ. We shall draw also the lines Ol and Oq in the plane POZ, line Oq being perpendicular to OZ, and Ol at an angle $\theta/2$ with Oq. The line Ol therefore bisects the external angle $-ZOP$. If now we consider the beam scattered in the direction OP, all the rays scattered from the element of the electron included between the planes l and $l + dl$ are in the same phase at P.

The amplitude of the electric vector at P due to the rays scattered by this element is, in accordance with expression (10),

$$\eta dl \cdot A \frac{\eta}{\mu} \cdot \sin \alpha / LC^2,$$

where η is the charge and μ the mass of the electron per unit distance along Ol, A is the amplitude of the electric vector of the incident beam, and as before L is the distance OP. If $2\pi\delta/\lambda$ is the phase of the ray at P scattered from the element of the electron at $l = 0$ at a given instant, the electric intensity at that instant of the ray scattered from any element to P is

$$\frac{A\eta^2}{\mu} \frac{dl}{LC^2} \sin \alpha \cdot \cos \frac{2\pi}{\lambda} \left(\delta - 2l \sin \frac{\theta}{2} \right),$$

and the electric intensity due to the whole electron is

$$R_{L, a, \theta} = \frac{A\eta^2}{\mu} \frac{\sin \alpha}{LC^2} \int_{-a}^{a} \cos \frac{2\pi}{\lambda} \left(\delta - 2l \sin \frac{\theta}{2} \right) dl$$

$$= \frac{A\eta^2 \lambda}{2\pi\mu LC^2} \cdot \frac{\sin \alpha}{\sin \theta/2} \cdot \sin \left(\frac{4\pi a}{\lambda} \sin \frac{\theta}{2} \right) \cos \frac{2\pi\delta}{\lambda}.$$

Here, as before, a represents the radius of the electron. The amplitude is obviously the value of this quantity when $\cos (2\pi\delta/\lambda) = 1$, and the intensity of the ray scattered ot P by the electron is therefore

$$I_{L, a, \theta} = cA^2_{L, a, \theta}$$

$$= \frac{cA^2\eta^4\lambda^2}{4\pi^2\mu^2L^2C^4} \cdot \frac{\sin^2 \alpha}{\sin^2 \theta/2} \sin^2 \left(\frac{4\pi a}{\lambda} \sin \frac{\theta}{2} \right).$$

Since $2a\eta = e$, $2a\mu = m$ and $cA^2 =$ the intensity I of the incident beam, the first factor of this expression becomes

$$\frac{Ie^4}{m^2L^2C^4} \left(\frac{\lambda}{4\pi a} \right)^2.$$

When α is expressed in terms of θ and ξ we obtain

$$\cos \alpha = \sin \theta \cos \xi,$$

i. e.,

$$\sin \alpha = \sqrt{1 - \sin^2 \theta \cos^2 \xi}.$$

We may therefore write:

$$I_{L,\xi,\theta} = \frac{Ie^4}{m^2L^2C^4}\left(\frac{\lambda}{4\pi a}\right)^2 \sin^2\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)\frac{1-\sin^2\theta\cos^2\xi}{\sin^2(\theta/2)}.$$

The intensity of the beam scattered by an electron at an angle θ with an unpolarized incident beam is the average of this quantity for all values of ξ, or

$$\begin{aligned} I_{L,\theta} &= \frac{1}{2\pi}\int_0^{2\pi} I_{L,\xi,\theta}\, d\xi \\ &= \frac{Ie^4}{2m^2L^2C^4}\left(\frac{\lambda}{4\pi a}\right)^2 \sin^2\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)\frac{(\cos^2\theta+1)}{\sin^2(\theta/2)}. \end{aligned} \tag{14}$$

The total energy scattered in unit time by the electron is given by the quantity

$$\begin{aligned} E_s &= \int_0^{\pi} I_{L,\theta}\cdot 2\pi L^2 \sin\theta d\theta \\ &= \frac{\pi Ie^4}{m^2C^4}\left(\frac{\lambda}{4\pi a}\right)^2\cdot\int_0^{\pi}\sin^2\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)\frac{(\cos^2\theta+1)}{\sin^2(\theta/2)}\sin\theta d\theta. \end{aligned} \tag{15}$$

This integral may be evaluated either graphically or by means of a series. To integrate by series, substitute $\theta/2 = x$ and $4\pi a/\lambda = b$. The integral factor then becomes:

$$\int_0^{\pi/2}\sin^2(b\sin x)\,\frac{4\sin^4 x - 4\sin^2 x + 2}{\sin^2 x}\cdot 2\sin x\cos x\cdot 2\,dx.$$

Writing $b\cdot\sin x = z$, this reduces to

$$8\int_0^{b}\sin^2 z\left(\frac{2z^3}{b^4}-\frac{2z}{b^2}+\frac{1}{z}\right)dz.$$

If $\sin^2 z$ is expanded into the series

$$\sin^2 z = z^2 - \left(\frac{1}{3!}+\frac{1}{3!}\right)z^4 + \left(\frac{1}{5!}+\frac{1}{3!3!}+\frac{1}{5!}\right)z^6 - \cdots,$$

each term may be integrated separately, the result being,

$$8b^2\{\alpha - \beta b^2 + \gamma b^4 - \cdots\},$$

where

$$\alpha = \frac{1}{3} = .33333,$$

$$\beta = \left(\frac{1}{4}-\frac{1}{3}+\frac{1}{4}\right)\left(\frac{1}{3!}+\frac{1}{3!}\right) = .05556,$$

$$\gamma = \left(\frac{1}{6}-\frac{1}{4}+\frac{1}{5}\right)\left(\frac{1}{5!}+\frac{1}{3!3!}+\frac{1}{5!}\right) = .00519,\ 5,$$

$$\delta = \left(\frac{1}{8}-\frac{1}{5}+\frac{1}{6}\right)\left(\frac{1}{7!}+\frac{1}{5!3!}+\frac{1}{3!5!}+\frac{1}{7!}\right) = .00029,\ 10,$$

ϵ = .00001, 076 η = .00000, 00053, 5,

ζ = .00000, 0280 θ = .00000, 00000, 77.

The total energy scattered by the electron in unit time is therefore

$$E_s = \frac{8\pi I e^4}{m^2 C^4}\left\{\alpha - \beta\left(\frac{4\pi a}{\lambda}\right)^2 + \gamma\left(\frac{4\pi a}{\lambda}\right)^4 - \cdots\right\}. \tag{16}$$

When the wave-length is large compared with the radius of the electron, all terms after the first are negligible, in which case

$$(E_s/I)_{a/\lambda=0} = \frac{8\pi}{3}\frac{e^4}{m^2C^4},$$

as it should. Writing as before N as the number of electrons per unit mass, σ as the scattering coefficient per unit volume and ρ as the density, the mass scattering coefficient of a substance composed of flexible spherical electrons is

$$\frac{\sigma}{\rho} = \frac{8\pi e^4 N}{m^2 C^4}\left\{\alpha - \beta\left(\frac{4\pi a}{\lambda}\right)^2 + \gamma\left(\frac{4\pi a}{\lambda}\right)^4 - \cdots\right\}. \tag{17}$$

3. *To calculate the energy scattered by an electron in the form of a thin, flexible, circular ring of electricity.*

In order to account for the electromagnetic mass of a ring electron, Webster[1] and Davisson[2] have shown that the ring must be very thin compared with its diameter. As a result of this fact, the inertia of any element of the ring is practically dependent only upon those parts of the ring immediately adjacent to it. Unless the wave-length is much smaller than the diameter of the electron, therefore, it is permissible to treat the mass of an element of the electronic ring as having a definite value.

Difficulties arise in this calculation, however, from the fact that the electromagnetic mass of an element differs according as the element is accelerated perpendicular or parallel to the tangent to the electronic ring at that point. The effective perpendicular mass depends also upon the speed with which the ring of electricity is rotating. For purposes of calculation I have assumed that the speed with which the electricity in the ring is moving is small compared with the velocity of light, and also that the mass of an element of the electron is independent of the direction of the acceleration. Admittedly the latter assumption makes the calculated value of the scattering only approximate, but it is probable that except possibly for the hardest γ-rays the approximation is close. I have further assumed, as in the case of the sphere, that the ring electron

[1] D. L. Webster, *loc. cit.*

[2] Davisson, *loc. cit.*

is flexible, *i. e.*, that the different parts of the charge are free to move relatively to each other. As was pointed out when the flexible sphere was considered, for comparatively long waves such an electron will scatter in practically the same manner as will a rigid electron which is free to rotate about any axis; for very short waves, however, the scattering by the two types of electron will not be exactly the same. The expression derived below for the scattering by a ring electron may therefore be relied upon for any except very short γ-rays.

In Fig. 7, imagine a beam of γ-rays going in the direction $-ZOZ$, and being scattered by an electron of radius a, represented by the heavy ring. Let us first determine the energy scattered in the direction OP, at

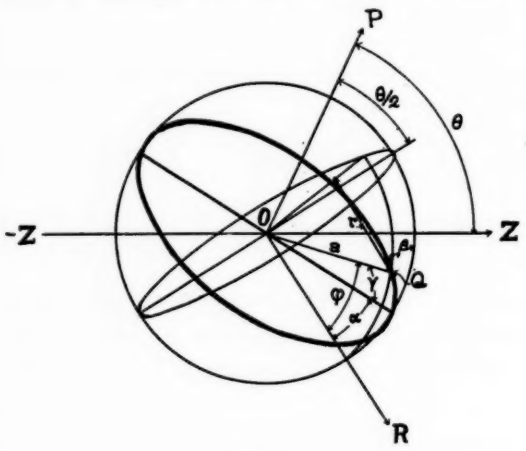

Fig. 7.

an angle θ with OZ. As is evident from the figure, the plane of the electronic ring makes a dihedral angle β with the plane ZOP, and the line of intersection of these two planes makes an angle α with the line OR bisecting the external angle $-ZOP$.

Consider first the energy scattered toward P due to the component of the electric vector which is perpendicular to the plane of the paper. If L is the distance, in the direction OP, at which the scattered radiation is evaluated, the electric displacement due to an element of the electron at $Q(a, \alpha, \beta, \gamma)$ is, in accordance with expression (10),

$$\frac{\eta a d\gamma \cdot A_1 \frac{\eta}{\mu}}{LC^2} \cdot \cos \frac{2\pi}{\lambda}\left(\delta - 2r \sin \frac{\theta}{2}\right).$$

In this statement, η is the charge and μ the mass per unit length of the circumference of the ring, A_1 is the amplitude of the electric vector

perpendicular to the plane of the paper, r is the distance from Q to a plane drawn through O perpendicular to OR, and $2\pi\delta/\lambda$ is the phase angle of a ray scattered to P from this plane.

The displacement at P due to the whole electron is therefore

$$\frac{A_1\eta^2 a}{\mu LC^2}\int_0^{2\pi}\cos\frac{2\pi}{\lambda}\left(\delta - 2r\sin\frac{\theta}{2}\right)d\gamma.$$

This quantity is obviously a maximum when $\delta = 0$, so the amplitude at P due to the rays scattered by the whole electron is

$$\frac{A_1\eta^2 a}{\mu LC^2}\int_0^{2\pi}\cos\frac{4\pi}{\lambda}\left(r\sin\frac{\theta}{2}\right)d\gamma,$$

and the corresponding intensity is

$$\frac{cA_1^2\eta^4 a^2}{\mu^2L^2C^4}\left\{\int_0^{2\pi}\cos\frac{4\pi}{\lambda}\left(r\sin\frac{\theta}{2}\right)d\gamma\right\}^2. \tag{18}$$

This expression represents the intensity at P due to an electron with the particular orientation defined by the values of α and β. The probable intensity at P due to polarized rays scattered by an electron at O is the average of this quantity for all values of α and β; *i. e.*,

$$\frac{cA_1^2\eta^4 a^2}{\mu^2L^2C^4}\int_0^{\pi}\frac{d\alpha}{\pi}\int_0^{\pi}\frac{d\beta}{\pi}\left\{\int_0^{2\pi}\cos\frac{4\pi}{\lambda}\left(r\sin\frac{\theta}{2}\right)d\gamma\right\}^2.$$

In a similar manner, the probable intensity at P due to the component of the incident electric vector which is parallel with the plane of the paper is

$$\frac{cA_2^2\eta^4 a^2\cos^2\theta}{\mu^2L^2C^4}\int_0^{\pi}\frac{d\alpha}{\pi}\int_0^{\pi}\frac{d\beta}{\pi}\left\{\int_0^{2\pi}\cos\frac{4\pi}{\lambda}\left(r\sin\frac{\theta}{2}\right)d\gamma\right\}^2,$$

where A_2 is the component of the incident amplitude parallel to the plane of the paper. Since on the average $A_1 = A_2$, and since the intensity of the unpolarized incident beam is $I = c(A_1^2 + A_2^2)$, we may write as the intensity of the beam scattered to P by an electron at O traversed by an unpolarized γ-ray,

$$I_{L,\theta} = \frac{I\eta^4 a^2}{\pi^2\mu^2L^2C^4}\,\frac{(1+\cos^2\theta)}{2}\int_0^{\pi}d\alpha\int_0^{\pi}d\beta\left\{\int_0^{2\pi}\cos\frac{4\pi}{\lambda}(r\sin\theta/2)d\lambda\right\}^2.$$

Remembering that $2\pi a\eta = e$ and $\eta/\mu = e/m$, the intensity of the beam scattered at the angle θ by an electron is

$$I_{L,\theta} = \frac{Ie^4(1+\cos^2\theta)}{8\pi^4m^2L^2C^4}\int_0^{\pi}d\alpha\int_0^{\pi}d\beta\left\{\int_0^{2\pi}\cos\frac{4\pi}{\lambda}(r\sin\theta/2)d\gamma\right\}^2. \tag{19}$$

To evaluate this expression it is necessary to write r in terms of α, β and γ. In Fig. 7,

$$r = \alpha\cos\varphi$$

and

$$\cos\varphi = \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma.$$

Thus

$$r = a\,(\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma).$$

The first integral of equation (19) then becomes

$$F_1 = \int_0^{2\pi} \cos\frac{4\pi a}{\lambda}\left\{\sin\frac{\theta}{2}\,(\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma)\right\} d\gamma.$$

Substitute

$$k = \frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\cos\alpha,$$

and

$$l = \frac{4\pi a}{\lambda}\sin\theta/2\sin\alpha\cos\beta.$$

Then

$$F_1 = \int_0^{2\pi} \cos(k\cos\gamma - l\sin\gamma)d\gamma.$$

We may write

$$k\cos\gamma - l\sin\gamma = m\sin(\gamma + \Delta),$$

where m is the maximum value of $k\cos\gamma - l\sin\gamma$, *i. e.*,

$$m = \sqrt{k^2 + l^2}$$

$$= \frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\sqrt{1 - \sin^2\alpha\sin^2\beta},$$

and Δ is the appropriate phase angle. With this substitution,

$$F_1 = \int_0^{2\pi} \cos\{m\sin(\gamma + \Delta)\}d\gamma.$$

Since the integration extends from 0 to 2π, the value of Δ is immaterial, and may therefore be put to equal zero. The integral then becomes,

$$F_1 = \int_0^{2\pi} \cos(m\sin\gamma)\,d\gamma$$

$$= 2\pi\cdot\frac{1}{\pi}\int_0^{\pi} \cos(m\sin\gamma)\,d\gamma$$

$$= 2\pi\cdot J_0(m),$$

where

$$J_0(m) = 1 - \frac{m^2}{2^2} + \frac{m^4}{2^2\cdot 4^2} - \frac{m^6}{2^2\cdot 4^2\cdot 6^2} + \cdots,$$

i. e., Bessel's J function of the zero order. Thus

$$F_1 = 2\pi J_0\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\sqrt{1 - \sin^2\alpha\sin^2\beta}\right).$$

The second integral of expression (19) may be written

$$F_2 = \int_0^\pi F_1^2 d\beta = \int_0^\pi \left\{ 2\pi J_0\left(\frac{4\pi a}{\lambda} \sin\frac{\theta}{2} \sqrt{1 - \sin^2\alpha \sin^2\beta} \right) \right\}^2 d\beta.$$

By substituting

$$\frac{4\pi a}{\lambda} \sin \theta/2 = k$$

and $\sin \alpha = l$ this is reduced to the form

$$F_2 = 4\pi^2 \int_0^\pi J_0^2(k \sqrt{1 - l^2 \sin^2 \beta}) d\beta.$$

The integral can be evaluated by expansion into a series of the form

$$J_0^2(x) = 1 - Ax^2 + Bx^4 - Cx^6 + \cdots,$$

and integrating term by term. In this series

$$A = \frac{1}{2^2} + \frac{1}{2^2},$$

$$B = \frac{1}{2^2 \cdot 4^2} + \frac{1}{2^2 \cdot 2^2} + \frac{1}{2^2 \cdot 4^2},$$

$$C = \frac{1}{2^2 \cdot 4^2 \cdot 6^2} + \frac{1}{2^2 \cdot 4^2 \cdot 2^2} + \frac{1}{2^2 \cdot 2^2 \cdot 4^2} + \frac{1}{2^2 \cdot 4^2 \cdot 6^2},$$

$$D = \frac{1}{2^2 \cdot 4^2 \cdot 6^2 \cdot 8^2} + \frac{1}{2^2 \cdot 4^2 \cdot 6^2 \cdot 2^2} + \frac{1}{2^2 \cdot 4^2 \cdot 2^2 \cdot 4^2} + \frac{1}{2^2 \cdot 2^2 \cdot 4^2 \cdot 6^2} + \frac{1}{2^2 \cdot 4^2 \cdot 6^2 \cdot 8^2},$$

etc.

Performing the integration we obtain

$$F_2 = 4\pi^3 \{ M + Nl + Ol^2 + Pl^3 + \cdots \},$$

where

$$M = J_0^2(k),$$
$$N = \tfrac{1}{2}(Ak^2 - 2Bk^4 + 3Ck^6 - \cdots),$$
$$O = \tfrac{1}{2} \cdot \tfrac{3}{4}(Bk^4 - 3Ck^6 + 6Dk^8 - 10Ek^{10} + \cdots),$$
$$P = \tfrac{1}{2} \cdot \tfrac{3}{4} \cdot \tfrac{5}{6}(Ck^6 - 4Dk^8 + 10Ek^{10} - 20Fk^2 + \cdots),$$

etc.

The third integral is

$$F^3 = \int_0^\pi F_2 d\alpha = 4\pi^3 \int_0^\pi (M + N \sin^2\alpha + 0 \sin^4\alpha + \cdots) d\alpha$$
$$= 4\pi^4 \left(M + \tfrac{1}{2} N + \tfrac{1}{2} \cdot \tfrac{3}{4} O + \tfrac{1}{2} \cdot \tfrac{3}{4} \cdot \tfrac{5}{6} P + \cdots\right).$$

Substituting the above values of M, N, O, etc., this may be written

$$F^3 = 4\pi^4(1 - \alpha k^2 + \beta k^4 - \gamma k^6 + \cdots),$$

where

$\alpha = (1 - \frac{1}{4})A = .37500,$

$\beta = (1 - \frac{2}{4} + \frac{1}{4}\cdot\frac{9}{16})B = .06006, 0,$

$\gamma = (1 - \frac{3}{4} + 3\cdot\frac{1}{4}\cdot\frac{9}{16} - \frac{1}{4}\cdot\frac{9}{16}\cdot\frac{25}{36})C = .00498, 48,$

$\delta = (1 - \frac{4}{4} + 6\cdot\frac{1}{4}\cdot\frac{9}{16} - 4\cdot\frac{1}{4}\cdot\frac{9}{16}\cdot\frac{25}{36} + \frac{1}{4}\cdot\frac{9}{16}\cdot\frac{25}{36}\cdot\frac{49}{64})D = .00025, 060,$

$\epsilon = (1 - \frac{5}{4} + 10\cdot\frac{1}{4}\cdot\frac{9}{16} - 10\cdot\frac{1}{4}\cdot\frac{9}{16}\cdot\frac{25}{36} + 5\cdot\frac{1}{4}\cdot\frac{9}{16}\cdot\frac{25}{36}\cdot\frac{48}{64}$
$- \frac{1}{4}\cdot\frac{9}{16}\cdot\frac{25}{36}\cdot\frac{49}{64}\cdot\frac{81}{100})E = .00000, 84241,$

$\zeta = .00000, 02023, 6,$

$\eta = .00000, 00036, 51,$

$\theta = .00000, 00000, 5056.$

The scattering at the angle θ is therefore

$$(20)\quad I_{L,\theta} = \frac{Ie^4(1 + \cos^2\theta)}{2m^2L^2C^4}\left\{1 - \alpha\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)^2 + \beta\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)^4 - \cdots\right\}.$$

The rate at which energy is scattered by an electron is obtained by integrating this expression over the surface of a sphere of radius L. That is

$$E_s = \int_0^\pi I_{L,\theta}\cdot 2\pi L^2 \sin\theta d\theta,$$

and since

$$\frac{\sigma}{\rho} = \frac{N}{I}E_s,$$

$$\frac{\sigma}{\rho} = \frac{Ne^4}{2m^2C^4}\int_0^\pi (1 + \cos^2\theta)\sin\theta\left\{1 - \alpha\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)^2 + \beta\left(\frac{4\pi a}{\lambda}\sin\frac{\theta}{2}\right)^4 - \cdots\right\}d\theta.$$

If for $\sin^2(\theta/2)$ we substitute $1/2(1 - \cos\theta)$, this expression is immediately integrable, and we obtain for the mass scattering coefficient,

$$(21)\quad \frac{\sigma}{\rho} = \frac{8\pi}{3}\frac{Ne^4}{m^2C^4}\left(1 - a\left(\frac{a}{\lambda}\right)^2 + b\left(\frac{a}{\lambda}\right)^4 - c\left(\frac{a}{\lambda}\right)^6 + \cdots\right),$$

where

$a = \frac{3}{4}(8\pi^2)(1 + \frac{1}{3})\alpha = 29.60881,$

$b = \frac{3}{4}(8\pi^2)^2(1 + \frac{1}{3} + \frac{1}{3} + \frac{1}{5})\beta = 524.1827,$

$c = \frac{3}{4}(8\pi^2)^3(1 + \frac{1}{3} + \frac{3}{3} + \frac{3}{5})\gamma = 5{,}397.801,$

$d = \frac{3}{4}(8\pi^2)^4(1 + \frac{1}{3} + \frac{6}{3} + \frac{6}{5} + \frac{1}{5} + \frac{1}{7})\delta = 35{,}619.04,$

$e = \frac{3}{4}(8\pi^2)^5(1 + \frac{1}{3} + \frac{10}{3} + \frac{10}{5} + \frac{5}{5} + \frac{5}{7})\epsilon = 162{,}501.7,$

$$f = \tfrac{3}{4}(8\pi^2)^6(1 + \tfrac{1}{3} + \tfrac{1}{3^5} + \tfrac{1}{5^5} + \tfrac{1}{5^5} + \tfrac{1}{7^5} + \tfrac{1}{7^5} + \tfrac{1}{9})\zeta = 541{,}970.2,$$

$g = 1{,}377{,}792,$	$n^1 = 3{,}717{,}000,$
$h = 2{,}757{,}220,$	$o^1 = 2{,}356{,}000,$
$i = 4{,}455{,}520,$	$p^1 = 1{,}334{,}000,$
$j = 5{,}935{,}500,$	$q^1 = 682{,}000,$
$k^1 = 6{,}632{,}700$	$r^1 = 318{,}000,$
$l^1 = 6{,}311{,}200,$	$s^1 = 136{,}000,$
$m^1 = 5{,}182{,}000,$	$t^1 = 54{,}000.$

The right hand member of this equation is convergent for all values of a/λ, but the convergence is very slow when λ approaches equality with a. The values of σ/ρ calculated according to this expression for different values of λ/a are shown in Fig. 2 by the solid part of curve *III*.

Elementary considerations suffice to determine the manner in which the scattering by a ring electron depends upon the wave-length when the frequency is very high. If we consider waves shorter than the diameter of the electron, it is apparent that the length of the arc of the ring which may be considered to vibrate as a unit due to the action of the incident beam will be proportional to the wave-length of the incident rays. The amplitude of the beam scattered by such a unit will therefore, by equation 10, be proportional to λe, and the intensity to $\lambda^2 e^2$. Since, however, the total number of such units in each electron will be inversely proportional to the wave-length, the intensity of the beam scattered by the whole electron will be proportional to $\lambda^2 e^2/\lambda$, *i. e.*, proportional to the wave-length. The solid part of curve *III* (Fig. 2) shows, as we should expect, that this relation holds approximately even for waves considerably longer than the diameter of the electron. I have therefore extrapolated curve *III* according to this law for values of λ/a too small for the practical application of formula 21, indicating these approximate values by the broken part of the curve.

RESEARCH LABORATORY,
WESTINGHOUSE LAMP COMPANY,
March 17, 1919.

[1] These values were determined by an approximation formula.

A FURNACE TEMPERATURE REGULATOR.

BY WALTER P. WHITE AND LEASON H. ADAMS.

SYNOPSIS.—By making the heating coil of an electric furnace one arm of a wheatstone bridge, and combining this with a galvanometer regulator, thus keeping constant the resistance of the coil, we can, regardless of variations in the current supply, and with no attention, maintain constant the temperature of furnaces not too directly influenced by the temperature of the room, or where the surrounding air is kept constant. The power available in this regulator is relatively very great indeed; nothing has to be inserted within the furnace cavity, and the lag is practically nothing; the regulator is often almost at its best under conditions most unfavorable to other regulators. It has held a small furnace constant to 0.1° for hours at temperatures from 500° to 1400°.

THIS paper describes a temperature regulator for electric furnaces, which has extraordinary sensitiveness and is effective under extreme conditions.

We had already succeeded in automatically regulating to about 5° at 1400° by letting a thermocouple recorder make electric contacts which actuated a polarized relay controlling a larger magnet which controlled the current. But we wished to regulate to about 0.1°, or 50 times as close, and at the same time to change the heating current by 10 per cent., in order to minimize the amount of attention required from the observer. This change in the heating current was found to change the furnace temperature so rapidly that to prevent fluctuations of 0.1° an adjustment nearly once a second was needed. Since the sensitiveness of a galvanometer falls off rapidly as the period is shortened, this combination of sensitiveness and speed required hundreds of times the energy that could be obtained from a platinum thermocouple.

This energy was obtained by drawing on the heating current of the furnace. The platinum furnace coil was made one arm of a wheatstone bridge, Fig. 1, so that the regulation was really by a resistance thermometer with a current of from 12 to 18 amperes. This method of regulating by controlling the coil temperature has, besides the great supply of energy, two other advantages. It avoids all necessity of introducing appliances into the furnace cavity, and it eliminates entirely the lag between heater and regulator, since the two are now identical.[1]

[1] Any device employing a wheatstone bridge has also the advantage of being more easily made to use the galvanometer as a null instrument—a thing necessary in work of high precision.

It has one important disadvantage; the temperature of the furnace is nearly always somewhat influenced by that of the room, so it may vary slightly, even when the coil temperature is maintained constant.

These peculiarities determine the most favorable conditions for this type of regulator. For furnaces whose small cavities render undesirable the introduction into them of any apparatus; for those whose small mass causes a quick response to current changes, and so calls for absence of lag, and for quickness, that is, sensitiveness, in the regulator, this type may have superior advantages. These conditions are more apt to occur in work at relatively high temperatures, and such temperatures also impair the efficiency of this regulator less than that of some others. Where the furnace is more capacious, or more massive, and hence adapted to more sluggish regulation, there is less need for the present regulator, and if the ends of the furnace contribute a considerable portion of its surface other regulators may even be more satisfactory.

Adjustments or tests of these regulators are very tedious if the furnace is large, and doubly so, of course, if the room temperature requires exact manipulation for the test. The approximate value of the effect of room temperature on one furnace was rather rapidly determined, as follows: First the constant rate, V, at which the furnace cooled with heating shut off, was observed, as well as φ, the thermal head, or temperature difference causing heat flow; that is, the difference between furnace and room. Then by Newton's Law of Cooling, we have $K_1 = V/\varphi$, where K_1 is the thermal leakage modulus of the furnace to the room. Second, the way was observed in which the furnace temperature changed when, after this had become constant, the coil was suddenly brought to a different temperature and held there. Then K_2, the modulus of the coil to the furnace, is obtained by applying the formula

$$\theta = \theta_s + (\theta_0 - \theta_s)e^{-K_2 t},$$

where θ is furnace temperature; and θ_0 and θ_s are its initial and final values, with θ_s also the second value of the coil temperature. If we then put θ_1, θ_2, θ_3, for the temperatures of coil, furnace, and room respectively, it is clear that the furnace in equilibrium will reach a temperature such that the heat coming to it from the coil equals that which it loses to the air, or that

$$K_2(\theta_1 - \theta_2) = K_1(\theta_2 - \theta_3);$$

that is

$$\theta_2 = \frac{K_1\theta_3 + K_2\theta_1}{K_1 + K_2},$$

so, as may be seen by simple differentiation, a given change in the room (θ_3) produces $K_1/(K_1 + K_2)$ times as much change in the furnace (θ_2).

This calculation gives too high results, since when the furnace is heated no heat escapes from it by way of the heating wire, while it does so escape during the determination of K_1. It is evident that if the heating coil is, instead of a wire, a flat strip of metal practically covering all the surface of the furnace, there would be almost no effect from the room. By combining with the heater wire a wire of copper or nickel exposed to the air a large amount of compensation can be obtained for the room effect. If the room is cooler the exposed wire is cooler; in order to make the combined resistance the same the heater wire must run warmer than usual; and thus it overcomes the cooling effect of the room. The difficulty with such an arrangement is, first, the time required to adjust for correct compensation, and second, the effect of lag, which tends to throw the balance out, except for slow changes.

In the furnace which we tested for K_1 and K_2 the indications were satisfactory, but the end effects, which were complicated by separately controlled coils, proved to be a disturbing factor. In our high temperature platinum-wound furnace, where the ends were small, and the coil adhered closely to the chamber wall, no effect from the room temperature was ever noticed, and the furnace, after once reaching equilibrium, usually held to 0.1° for several hours, even at 1400°. The room, however, seldom varied over 5°.

Since an account of this regulator was first presented in public, by Mr. Adams (at the Washington meeting of the Physical Society, April, 1913) several experimenters have used the principle of a heater-thermometer-regulator in oil baths. This is an appropriate use for it, for if the wire is in contact with the oil K_2 is very large, and the room temperature disturbance is therefore small, especially if K_1 can be kept small by covering the top.

As Fig. 1 indicates, some mechanical arrangement is necessary to cause the current-regulating switches to move according to the changes in the position of the galvanometer boom. This can very readily be accomplished in one of several fairly familiar ways. The easiest, perhaps, is the one suggested in the first paragraph of this paper, namely, having the boom pressed up or down at intervals so as to either strike or miss a contact maker (or either one of a pair) which controls a suitable relay. A light motor-driven mechanism pressing the boom every second or so is then the only special machinery required. The Leeds and Northrup Co. furnish a stock instrument which operates in this way. They also offer a form in which the switches are moved by the motor, without magnets. This is a little tardy in its action, since the switch setting for a given pressing of the boom is not made till the next pressing occurs.

But if one of the ratcheting rheostats now available is used, the single step can be made smaller and the period does not need to be so short. If we had planned to use such a rheostat our own time requirement would not have been so exacting as it was. Our own mechanical arrangement[1] utilizes the power and certainty of the motor to operate the switch, but gives nearly the promptness of a magnet, so that a single switch is enough

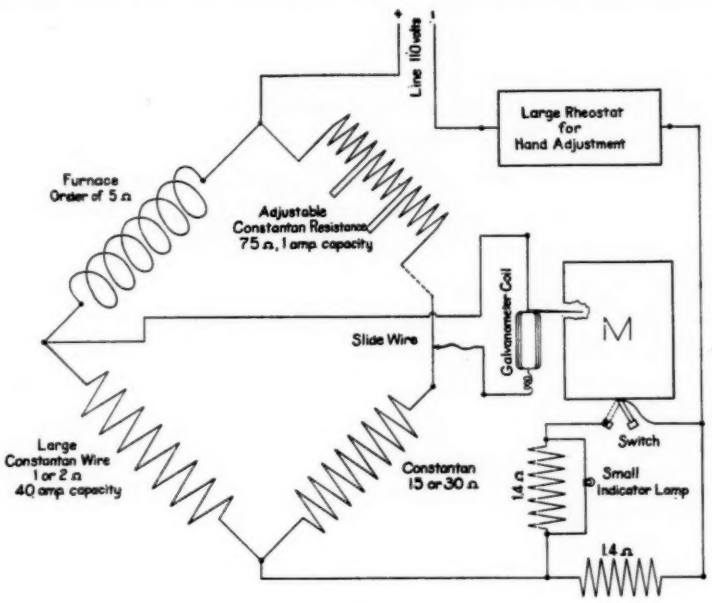

Fig. 1.

for the regulation. The change in switch setting due to one pressing of the boom produces a large effect on the galvanometer before the next pressing occurs. This instrument is not represented because Mr. Shaw now thinks he could get as great efficiency with a simpler design, and no such design has been completely worked out.

Our galvanometer coil was an old wooden-spooled affair, of the type much used in the nineties, provided with a more modern magnet. With a 1-second period, auxiliary oil damping was needed. The boom was 5 cm. long, and a shift of 0.1 mm. at its end was enough to cause a change of the switch setting. This shift was produced by 24 microvolts across terminals. For 14 amperes (about the average current) 24 microvolts corresponded to a change of 0.004°, so the possibilities of the arrangement in the way of sensitiveness are, as was to be expected, in excess of any conceivable requirement. Indeed, it is clear that since the

[1] Designed by Mr. C. M. Shaw, Master Mechanic of the Laboratory.

sensitiveness of an underdamped galvanometer varies as the square of the period, for a period of 3 seconds or more this galvanometer would adjust to 0.1° with a silver-constantan couple (5 microvolts per 0.1°), or with a smaller resistance thermometer. This is, however, an arrangement for lower temperatures and larger furnaces, and is one which abandons the special feature which this paper is written to describe.

Since this special feature, namely, operation by means of the furnace coil itself, calls for resistance variation with temperature, it is not so well adapted to nichrome coils, whose temperature coefficient is very small. Nevertheless, our own arrangement is apparently sensitive enough to work with them, especially where the period can be lengthened a little. We actually used, at 500°, a nickel manganese alloy of high coefficient, but do not feel justified in recommending it as satisfactorily free from liability to injury by oxidation, even at that temperature. Satisfactory alloys may be known, however, whose temperature coefficient is higher than that of ordinary nichrome, and there seems to be no doubt that such can be made. The loss of power in the other three arms of the wheatstone bridge can generally be made negligible if the galvanometer sensitiveness is comparable to ours. The device, in its present form, evidently is not applicable to alternating currents.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.,
March, 1919.

THE VARIATION IN SOUND INTENSITY OF RESONATORS AND ORGAN PIPES WITH BLOWING PRESSURE.

BY BERYL F. LOVE AND MARGARET K. DAWSON.

SYNOPSIS.—Quantitative measurements were taken to ascertain the relation between the sound intensity of wind-blown instruments and the blowing pressure. The intensities of sound emitted by a tone-variator resonator and an organ pipe were measured by a Rayleigh resonator while the blowing pressure was noted by means of a water manometer. Assumptions concerning the constancy of the pitch of the sound and permancy of the sound pattern appeared justified.

The measurements showed that the intensity of the sound varied directly with the blowing pressure for the tone-variator and gave nearly a direct relation for the organ pipe. A discussion of the theory indicated that only part of the energy of the air pressure was converted into sound.

THAT the intensity of sound emitted by an organ pipe becomes greater when blown more strongly is a fact easily perceived by the ear; but a quantitative estimation of the comparative intensities is not so readily determined because the ear is not trustworthy for such measurements. The present investigation was undertaken to secure quantitative data on the variation of sound intensity of organ pipes and

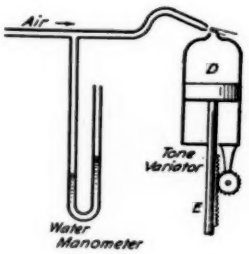

Fig. 1.

Showing arrangement for generating sound from a tone variator by means of compressed air.

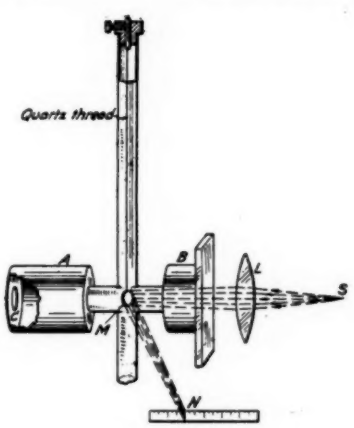

Fig. 2.

Rayleigh resonator used for measuring intensity of sound.

resonators when the blowing pressure was increased. The apparatus is pictured in Figs. 1 and 2.

The sound was generated by blowing compressed air across the mouth of a "tone variator" resonator,[1] the pressure of the air being measured by a water manometer. By adjusting the piston of the tone variator, a range of tones of varying pitch could be obtained. The intensity of the sound was measured by means of a modified Rayleigh resonator[2] shown in Fig. 2. In this instrument, a glass disc M, suspended by a quartz thread, was placed in the intercommunicating channel of a double resonator AB. When properly tuned to the external sound, a resonance resulted causing the disc to rotate through a small angle, the amount of rotation being noted by the deflection of a spot of light on the scale N after reflection from the disc. The deflections on the scale are proportional within a small per cent. error to the intensities of the sound.[3] The resonator was tuned by adjusting the length, and consequently the volume, of B, and by varying the size of the opening of the iris diaphragm at C.[4]

The procedure in taking measurements was as follows: The tone variator was blown by a steady air pressure and then adjusted in pitch until it gave a maximum deflection of the Rayleigh resonator. The air pressure was increased successively by small amounts and the rise in pitch[5] of the tone variator reduced each time to give a maximum deflection of the resonator. This was continued until the sound showed distortion due to overtones or other causes. Measurements taken in this way gave simultaneous values of blowing pressure and resultant sound intensity. To avoid disturbance of the standing waves of sound in the room, the observer was stationed in a closed compartment where observations could be taken through a window and the tone variator adjusted by means of a long steel rod.

It was assumed in this procedure that the intensities measured were comparable provided the interference pattern of the sound in the room remained constant. That this condition was fulfilled is explained in the following way. When a sound is generated, waves spread out from the source and, by successive reflections from the boundaries of the room, set up interferences that give stationary maxima and minima of sound. The Rayleigh resonator will give a maximum deflection when the opening of the iris diaphragm is at a node.[6] The response is less for other positions

[1] L. W. Stern, Zeitsch. f. Psychologie u. Physiologie der Sinnesorgane, Vol. 30, p. 422, 1902.

[2] Rayleigh, Phil. Mag., Vol. 14, p. 186, 1882.

[3] Watson, PHYS. REV., Vol. 7, p. 125, 1916.

[4] Rayleigh, Theory of Sound, Vol. 2, Sec. 310.

[5] Rayleigh, Phil. Mag., III., p. 462, 1877; XIII., p. 340, 1882. See also article by Mr. A. Mallock, Proc. of Royal Society, Ser. A, Vol. 95, p. 99, 1918. Describes experimental work leading to simple explanation of change of pitch of organ pipes with pressure.

[6] Rayleigh, Theory of Sound, Vol. II., Sec. 269a.

and becomes zero if the opening coincides with a loop. If a new arrangement of maxima and minima is set up, as would be the case if the pitch of the sound were changed, or if any object in the room were moved to a new position, the deflection of the resonator would probably change even though the intensity of the source of sound remained unaltered. If the pitch and arrangement of articles in the room remained constant as described, it was assumed that the interference pattern would not change when the pressure of the air blowing the tone variator increased but that the intensity of sound at each point in the room would increase in proportion to the pressure. This assumption receives support from some earlier work[1] where sound reflected into a room from successively increased layers of material gave corresponding deflections of a Rayleigh resonator what were directly proportional to the thicknesses of the layers.

It was further assumed that the pitch of the tone variator had the same value for each measurement if adjusted to give a maximum deflec-

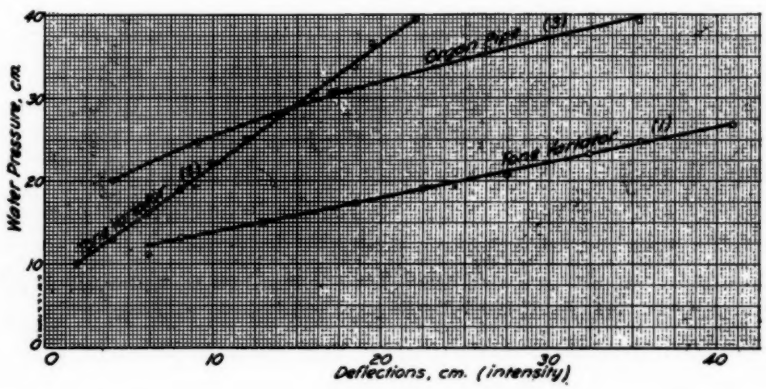

Fig. 3.

Curves showing the variation of sound intensity with blowing pressure for a tone variator and organ pipe.

tion of the Rayleigh resonator. This assumption was verified in later experiments by counting the number of beats made by the tone variator with a tuning fork for each measurement and finding them constant within experimental error. It was found that the adjustment for constant pitch could be made more easily by getting the maximum deflection of the resonator than by adjusting the tone variator to get the proper number of beats.

The results are given graphically in Fig. 3. Curve 1 shows the variation of the intensity of a tone variator with the blowing pressure. Since

[1] Watson, PHYSICAL REVIEW, Vol. VII., p. 287, 1916.

this appears to be a straight line, it indicates that the sound intensity varies directly with the pressure. Curve 2 gives data taken for the same tone variator with a rearrangement of apparatus. The data for Curve 2 are given in the following table.

Water Pressure.	Resonator Deflections.	Beats with Tuning Fork.	Reading of Tone Variator.
7.2 cm.	Readings uncertain		
10.0	1.9±0.1 cm.	3.08 per sec.	395
13.0	4.1	3.49	391
16.1	6.2	3.26	389
19.0	8.1	3.31	387
22.2	9.9	3.51	385
25.0	12.0±0.5	3.19	383
27.9	13.9	3.00	382
30.0	16.0	3.26	380
33.7	18.4	3.26	380
36.6	19.4	3.31	378
39.5	22.0±1.0	3.04	375

Inspection of the results shows that a steady tone was not obtained until the pressure increased to about 10 centimeters of water. The resonator deflections were not steady but responded quickly to the fluctuations in pitch and intensity of the tone variator. These fluctuations are due most probably to small variations in the pressure of the compressed air used for blowing. It required considerable patience to adjust the tone variator for a maximum deflection in view of these fluctuations. In the last column a record is given of the scale readings of the tone variator. They show that the pitch rises with increased pressure and that the volume of the tone variator must be increased to reduce the pitch to a fixed value. They indicate also the necessity of calibrating such instruments for a stated, constant blowing pressure. Curve 3 in Fig. 3 shows the results for an organ pipe giving a note of about 320 vibrations per second. A movable piston allowed an adjustment of pitch, but some difficulty was experienced in getting the pipe to sound properly. The smooth curve in this case indicates that the intensity of the sound varied regularly with the blowing pressure but not in direct proportion as shown for the tone variator.

These observed results are not what would be expected from the theory of the subject. Rayleigh[1] has shown that the energy per second in blowing a whistle is proportional to the pressure p and the volume v of the air blown per second. If all of this energy went into the production of sound, then the intensity of sound, I, could be written: $I = kpv$, where k is a constant. If it is assumed that the volume increases directly

proportional to p, I would become: $I = k_1 p^2$. Since, however, it was observed that $I = k_2 p$, the conclusion is drawn that not all the energy of the air goes into sound but only that portion obtained as if v were constant.

In conclusion, aside from the interesting fact shown by the results, it would appear of some practical advantage to know that the intensity of sound of a resonator or organ pipe varies almost directly with the blowing pressure.

The authors desire to acknowledge the guidance and assistance of Dr. F. R. Watson during the course of the investigation.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
March, 1919.

[1] Proc. of Royal Society, XXVI., p. 248, 1877.

THE DISTRIBUTION OF ENERGY IN THE SPECTRUM OF ERBIUM OXIDE.

BY W. S. MALLORY.

SYNOPSIS.—In the experiments described in this paper the statements of previous observers to the effect that the selective emission of erbium oxide is not due to volatilization but is a radiation from the solid itself are corroborated. The temperatures at which the bright bands appear, reach their maximum and disappear are measured. By detailed spectrophotometric measurements it is shown that at 1000° C. both the red and green groups of bands greatly exceed in intensity the radiation of similar portions of the spectrum of a black body at the same temperature.

INTRODUCTION.[1]

IT was discovered in 1864 by Bunsen[2] that didymium, when heated to incandescence did not give the continuous spectrum commonly seen when solids are heated, but a spectrum consisting of bright bands, superimposed upon a relatively weak continuous spectrum. The same phenomenon was discovered in the case of erbium by Bahr[3] in 1865. Neodymium, holmium and perhaps a few other rare earths have been found to give the banded emission spectra, although in a lesser degree. Another peculiarity in the case of these substances lies in the fact that their absorption spectra consist of a great number of very narrow bands. In some cases these absorption bands may very properly be spoken of as lines. The narrow banded absorption spectra are characteristic of these rare earths, both in solution and in the solid condition.

The present investigation was undertaken in part to determine, if possible, whether the peculiar emission spectrum of erbium oxide, when heated to incandescence, is a purely thermal radiation, as indicated by the excellent agreement, at the same temperature, in the position of the emission and the absorption bands, or whether it might not be a case of luminescence, excited perhaps by the short wave-lengths of the flame used for heating the specimen under observation.

Another purpose was to determine for different wave-lengths the

[1] A good summary of the work that has been done on the spectra of the rare earths may be found in an article in the Astrophysical Journal of September, 1907. "The Absorption and Emission Spectra of Neodymium and Erbium Compounds," by J. A. Anderson.

[2] Bunsen, Liebig's Annalen, CXXXI, 255, 1864.

[3] Bahr, Liebig's Annalen, CXXXV, 376, 1865.

relation between the intensity of the radiation from the oxide, and the intensity of the radiation from a black body at the same temperature.

I later made an approximate determination of the temperature at which the radiation in the region of the green band of the emission spectrum had the same intensity as the corresponding radiation from a black body at 1000° C.

SOME PRELIMINARY OBSERVATIONS.

In preparation for the investigation it seemed best to repeat a number of experiments upon which others have reported. The results were briefly as follows:

1. *The Emission Spectrum not a Flame Spectrum.*—Some erbium oxide powder was placed upon a small piece of quartz and heated in the Bunsen flame. The powder was directly opposite the middle of the slit of a spectrometer. Sodium in the flame caused a yellow line to appear the entire length of the slit. Lithium added to the flame caused a red line to show the entire length of the slit. The erbium spectrum did not extend above the solid; there was nothing like its spectrum coming from the gas immediately above the solid. This indicated that the emission was from the solid and not from the vapor near the solid.

2. *Identity of Emission from the Oxide and from a Phosphate Bead.*—There has been some difference of opinion as to whether the emission is the same from the oxide as from the phosphate. To determine this a small portion of powdered oxide was intensely heated in the oxy-hydrogen flame and finally fused down into a cream-colored bead, without the use of any flux. I mounted this bead before the slit of the collimator and immediately above it another sample in which a syrupy phosphorus pentoxide had been used as flux. The two specimens were in the same flame and seen at the same time, one above the other. The two spectra were identical; so far as I was able to judge the red band appeared in the same place and in the same manner. The green lines appeared identical in the two spectra. In one trial it seemed as though the green bands stood out a little more distinctly in the case of the specimen prepared with the flux. This appearance was not characteristic and was not very marked in the one case that was noted.

3. *Relation between Emission and Absorption.*—It has been recognized, almost from the first, that there is a very close agreement in both the positions and intensities of the emission and absorption bands. J. A. Anderson,[1] in the summary of his investigations, concluded that the

[1] Anderson, Astrophysical Journal, XXVI., p. 93, 1907.

emission is due to the oxide itself, and that it corresponds exactly to its absorption at the same temperature. The absorption of the solid changes with temperature, the change consisting in a widening of the bands, and in some cases, a shift toward the red, with an increase of temperature. Anderson further concluded that the absorption of the dry compounds is different for different compounds of the same element.

In the case of the oxide under consideration in the present paper the absorption bands at room temperature and the emission bands during incandescence were located visually with a spectrometer. To obtain the absorption spectrum the fused oxide was placed before the slit of the instrument and the light of a carbon arc was focused upon it. As will be seen from the following table and from the spectrum map at the bottom of Fig. 2 the absorption bands occur in six groups each group

TABLE I.

Absorption Bands at + 20° and Emission Bands at 1000° observed in a specimen of commercial Erbium Oxide.

Group.	Absorption.		Emission.	Group.	Absorption.		Emission.
	μ.	$1/\mu \times 10^3$.	μ.		μ.	$1/\mu \times 10^3$.	
1	.4180	2392	.4100		.5198	1924	.5135
(unresolved)	to	to	to	4	.5222	1915	to
	.4223	2368	.4250		.5260	1901	
					.5306	1885	.5360
—	.4361	2293	—		.5407	1849	.5360
					.5417	1846	
	.4534	2206	.4500		.5438	1839	to
2	.4571	2188		5	.5461	1831	
	.4611	2169	to		.5474	1827	
	.4655	2148	.4685		.5562	1798	.5555
	.4916	2035	.4885		.6400	1562	.6400
	.4936	2188	to		.6521	1534	
3	.4971	2169			.6532	1531	to
	.4978	2148	.5015		.6551	1526	
					.6656	1502	
					.6751	1481	.6750

corresponding approximately in position to one of the broader emission bands. The single band at .436 μ may perhaps be the only visible member of still another group which may coincide with a feeble emission band which escaped notice.

4. *Fluorescence and Emission.*—The oxide under investigation was excited to fluorescence by cathode rays in a vacuum tube. The spectrum, as had been noted by earlier students of the rare earths, was distinctly different from the spectrum obtained when the same specimen was heated to incandescence. A broad red band began at wave-length .6065 μ and merged into a bright yellow band at .5880 which extended to .5730. A green band began at .5605 and ended at .5450. A dark space followed and then another green band between .5380 and .5020. There was brightness again beginning at about .4950 but this gradually became less intense and ended at about .4730. These broad bands are likewise indicated in Fig. 2 for convenience of comparison with the regions of emission and absorption. The determination of the relations between these spectra lies beyond the scope of the present paper.

5. *Development of Selective Emission with increasing Temperatures.*—In order to get a general idea as to the growth of the emission spectrum with increasing temperatures, I placed some of the erbium oxide powder between two thin plates of clear quartz. In the midst of the powder I placed one of the junctions of a thermocouple made of Pt, Pt-Rh, wires. The couple was joined through the proper resistance with a Paul unipivot pyrometer, reading approximately in degrees centigrade. The appearance at different temperatures may be described as follows:

600° C. A broad faint haze in the yellow green, ending rather abruptly on the side toward the blue. No red discernible.

640° C. Red band clearly seen and more light in the green, but it ended abruptly as before.

680° C. Sufficient light so that the slit could be narrowed. The green bands began to stand out from the green haze, which served as a background.

770° C. A faint suggestion of another band in the blue.

800° C. The red continued to stand out well, although there was a faint continuous spectrum over the whole field.

930° C. Two faint bands seen beyond the green. In the red was a dark portion, as though there were two bands, separated from one another.

1000° C. No further question about there being varying degrees of intensity in the red. The continuous spectrum was more pronounced, yet all the bands showed well.

1120° C. The band appearing in the blue seemed to be of two parts, while in the violet there seemed to be a very dim band made up of three parts. At this temperature the continuous spectrum began to mask the bands.

1220° C. The red had spread into a much broader band. In the extreme violet another band could be dimly seen. The boundaries of the green bands could be seen distinctly. The other bands appeared as broad patches, slightly more intense than the continuous spectrum which had pretty completely masked them.

6. *Emission not Due to Excitation by Radiation of Short Wave-Lengths.*—In the article by J. A. Anderson it was suggested that the simplest and best way to settle the question as to whether the radiation is due to the oxide itself or to a surface layer of gas, formed by the action of the flame, would be to heat the oxide without using the flame. In order to make this test, and at the same time prevent the excitation of fluorescence by any ultra-violet radiation from the flame itself, I made a nickel box about 2 cm. in diameter and 7.5 cm. in depth. This box was heated by a blast lamp flame playing against the bottom and sides. The specimen to be examined was mounted at the end of a bent quartz rod, in such a manner that it could be quickly swung up out of the box and before the slit of the collimator. When heated in this manner the red and the green bands were seen just the same as when the specimen was heated by the flame directly. The nickel box was not white hot, and the bands persisted for several seconds after cooling had begun, due to removal from the box. Since performing the experiment with the nickel box I have heated specimens in the electric furnace to be described in a subsequent paragraph and have found the spectrum to be the same as when heating directly with the flame. This is taken to establish that the banded emission spectrum is not due in any way to peculiar properties of the flame but that it is a thermal effect and independent of the manner of heating.

THE DISTRIBUTION OF ENERGY IN THE EMISSION SPECTRUM.

The main purpose of the present investigation, as has been indicated in the opening paragraph of this paper, was to determine whether the emission in the bright bands exceeds that in the corresponding regions in the spectrum of a black body at the same temperature. If so, the well-known corollary to Kirchhoff's law; that no body can emit more radiation of a given wave-length than does a black body at the same temperature is inapplicable to these highly selective radiators.

The instrument employed was a spectrophotometer designed for the study of luminescence spectra.[1] It consists of Hilger spectrometer of the constant deviation type to which a second collimator is added.

[1]Nichols, Proc. Am. Philos. Soc., LVI., p. 262.

A Lummer-Brodhun cube (B, Fig. 1) introduces light from the two collimators C_1 and C_2 into the prism P and the observing telescope T.

The comparison lamp L is a ten-volt straight filament lamp moving along a photometer track in line with collimator C_2. A carrier for a small electric furnace F and the erbium oxide O, moves along another track which is perpendicular to the axis of C_1. It is thus possible to compare the radiation from either the interior of the furnace, or the

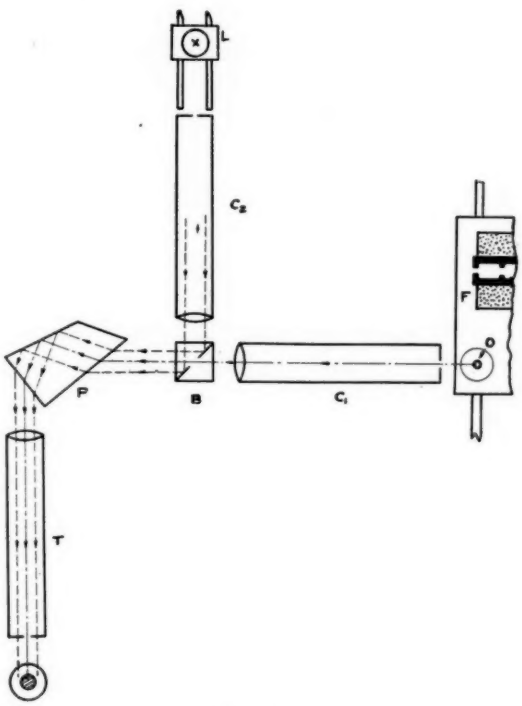

Fig. 1.

oxide, with the radiation from the comparison lamp by a method of substitution. If there is match of the two fields when the furnace is before the slit, and this match is destroyed when the oxide has replaced the furnace, there can be no doubt as to which gives the stronger radiation for that particular part of the spectrum.

Erbium oxide powder was mounted between two thin pieces of clear fused quartz, thus presenting a matte surface to the slit. This surface was about 1 cm. long and 0.6 cm. broad at the top, with an average thickness of 0.15 cm. A colorless hydrogen flame played around the quartz holder. When heated the powder would glow while the surrounding border of clear quartz would remain transparent and nearly

non-luminous. A slender quartz rod, fused to the bottom of the holder, supported the arrangement. I made two thermo-junctions out of platinum and platinum-rhodium wire. This wire had been carefully tested and found to give no E.M.F. due to lack of homogeneity. One of these couples was used to determine the temperature of the powder, a junction being placed in the midst of the powder. One junction of the other couple was immediately in front of the partition in the middle of the electric furnace the inner construction of which was similar to the well-known "Reichanstalt" black body. The tube was 45 cm. in length and had an internal diameter of 3 cm. I sighted against a disc placed in the middle of the tube. A number of diaphragms in the tube served to prevent air currents.

When heated it was impossible to make out the boundary of the disc, or the wires of the thermo-junction. Both thermocouples were connected through switches to a Wolff potentiometer, and it was also possible to join the couples in opposition through a Sullivan galvanometer of such a sensibility that a temperature difference of one degree, centigrade, was easily detected by the movement of the reflected spot of light. Since taking the data for the curves that appear in this paper, the junctions have been compared and found to agree to within 0.00002 volt throughout the temperature range, 700° C. to 1046° C. The temperatures as gotten from the potentiometer readings are probably not in error by more than two degrees at any time.

I tested for the uniformity of temperature over the surface of the oxide by means of a Morse thermal gage. This method while not very delicate was fairly conclusive, so far as the detection of considerable temperature differences is concerned. In the exploration of one specimen, for example, that had been used in several runs, the indicated temperature variations were from 827° C. to 840°, or a variation of 13°. Readings taken at different points varied no more however than when the successive settings were all made upon the same point. For both cases the average departure of the temperatures from the mean was about 1.8 per cent.

The use of clear quartz as a mounting in these experiments is essential. When heated in the flame up to 1200° C. it remains so nearly non-luminous that its visible spectrum is of a low order of intensity. Other advantages of the quartz are that it does not soften at the temperatures where the experiments were being carried on, and that at a high temperature it is a good conductor of heat. It is essential that the quartz be free of air bubbles, for although the clear quartz when heated emits little or no visible radiation, if it contains spots made up of an emulsion of quartz and air, these spots emit strongly, and this is true even when

the spots are at some distance from the heated portion of the tube or rod.

When making observations the two couples were commonly joined in opposition through the galvanometer. It was possible to keep the temperatures nearly constant. No readings were taken when the two temperatures differed by as much as ten degrees. In case of a lesser difference the readings were not used in the plotting of the curves except when the furnace temperature was the higher of the two. The furnace and the oxide were alternately placed before the slit. Three readings were made for each, at each wave-length. When working near the end of the visible spectrum it was sometimes difficult to make an exact setting but when the shift was made it was possible to tell whether the furnace or the oxide gave the more brilliant field.

In the spectrophotometric determinations the two collimator slits were set at equal width once for all, the slit-widths being as small as the intensity of the weaker regions of the spectrum would permit.

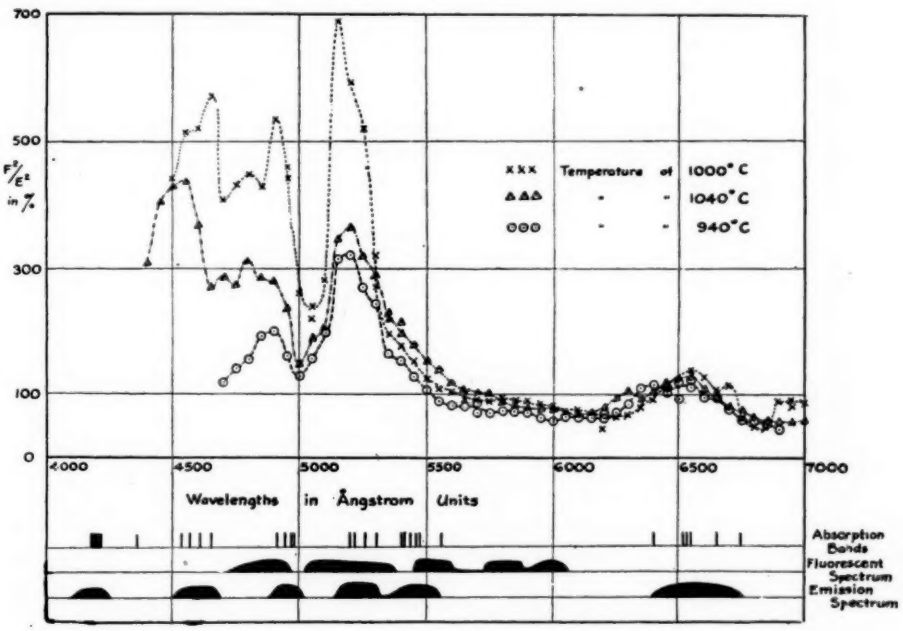

Fig. 2.

The carriage upon which the furnace and the incandescent oxide were mounted was brought to the position where light from the furnace entered collimator C_1. The place on the photometer bar where the light from the comparison lamp matched that from the furnace was determined when the thermocouples indicated equality of temperature between

furnace and oxide. The carriage was then immediately shifted so as to bring the oxide before the slit and the position of the lamp readjusted to a match. If the balance of temperatures was still satisfactory the readings on the photometer bar were accepted. Readings were made at intervals of 50 Ångström units.

TABLE II.

Emission of Erbium Oxide referred to that of a Black Body at the same Temperature.

Wave-length.	Relative Intensity.			Wave-length.	Relative Intensity.		
	940°.	1000°.	1040°.		940°.	1000°.	1040°.
.4400μ	—	—	3.06				
.4450	—	—	4.06	5750μ	0.70	0.85	0.98
.4500	—	4.42	4.29	5800	0.72	0.92	0.88
.4550	—	5.14	4.39	5850	0.70	0.90	0.84
.4600	—	5.20	3.68	5900	0.70	0.82	0.80
.4650	—	5.72	2.48	5950	0.62	0.82	0.80
.4700	1.20	4.08	2.86	6000	0.58	0.80	0.78
.4750	1.40	4.30	2.74	6050	0.62	0.72	0.70
.4800	1.55	4.50	3.11	6100	0.59	0.73	0.65
.4850	1.92	4.28	2.85	6150	0.60	0.70	0.70
.4900	2.00	5.35	2.79	6200	0.62	0.62	0.79
.4950	1.60	4.50	2.35	6250	0.65	0.71	0.94
.5000	1.34	2.60	1.48	6300	0.82	0.64	1.00
.5050	1.58	2.30	1.92	6350	1.05	0.82	0.92
.5100	2.10	2.80	2.12	6400	1.12	0.96	1.08
.5150	3.14	6.88	3.46	6450	1.08	1.15	1.18
.5200	3.20	5.90	3.65	6500	1.12	1.26	1.22
.5250	2.68	5.90	3.19	6550	1.12	1.36	1.28
.5300	2.41	2.68	2.68	6600	0.90	1.28	1.06
.5350	1.62	1.94	2.24	6650	0.92	1.02	0.92
.5400	1.51	1.79	2.04	6700	0.72	1.14	0.75
.5450	1.26	1.52	1.79	6750	0.57	0.62	0.72
.5500	1.04	1.22	1.44	6800	0.52	0.56	0.62
.5550	0.88	1.09	1.39	6850	0.48	0.44	0.58
.5600	0.80	1.02	1.18	6900	0.42	0.90	0.57
.5650	0.80	0.95	1.05	6950	—	0.87	0.56
.5700	0.75	0.85	1.00	7000	—	0.84	0.58

In this method of substitution if F is the distance on the photometer bar from the slit C_2 to the filament of the comparison lamp, when the fields are equally bright and the furnace is before the slit C_1 while E represents the corresponding distance, with the oxide before slit C; F^2/E^2 gives the ratio of emission of the oxide and the black body for the temperature in question and the wave-length under observation.

The results of a typical experiment, one of many, are given in Table II. and graphically in the curves in Fig. 2. The measurements were made

at 940°, 1000° and 1040° C. In the curves values of F^2/E^2, which give the relative intensities, are plotted as ordinates and wave-lengths as abscissæ. The results are quite different from what I had expected to find, it having seemed probable that the curves might approach a radiation approximately equal to that from a black body for the wave-lengths corresponding to the strong emission bands.

Below the curves showing the emission of the oxide when compared to that of the black body at the same temperature are shown the three spectra mentioned in an earlier paragraph. They were obtained from a sample of the erbium oxide prepared with a flux. The first one shows the absorption when the substance is placed before the slit and the light from a carbon arc is focused upon it. The second shows the fluorescent spectrum when it is excited by cathode rays in a vacuum tube. The third shows the emission spectrum when the same specimen is heated in the oxyhydrogen flame. The close agreement of the positions of the bands in the emission and the absorption spectra can easily be seen.

The range of temperatures employed in the spectrophotometric examination was so small, when we consider the necessarily somewhat uncertain temperature control in the use of the hydrogen flame that relative positions of the curves for 1000° and 1040° may perhaps be open to question. The evidence however seems strongly to favor the existence of a critical temperature of about 1000°.

To check the foregoing temperature determinations, the following modification in the method of mounting was tried. A piece of clear quartz tubing, 3 mm. internal diameter, was sealed at the lower end. Powder was tamped into the tube to a depth of 2.5 cm. The thermojunction was placed in the midst of the powder, opposite the middle of the slit. This tube was rotated about a vertical axis, thus heating the powder from all sides. Small quartz tubes enclosed the lead wires which at the upper end made contact with two rings of mercury, and through these rings the connection was made to the potentiometer and galvanometer, as before. The flame in this case rises about the tube containing the wires, which are heated to incandescence for two or three centimeters above the top of the powder.

With this new arrangement there is no doubt as to which of the two sources gives the more intense radiation. I have not had time to make complete runs with this set up of apparatus but I have examined the spectrum at those wave-lengths where the radiation is most intense and have found the effect to be of the same order of magnitude as shown in the curves.

A further check was obtained by determining the temperature at which the emission bands of the oxide would give the same radiation as the black body at 1000° C. In this experiment the furnace was kept at that temperature and readings were taken for several temperatures

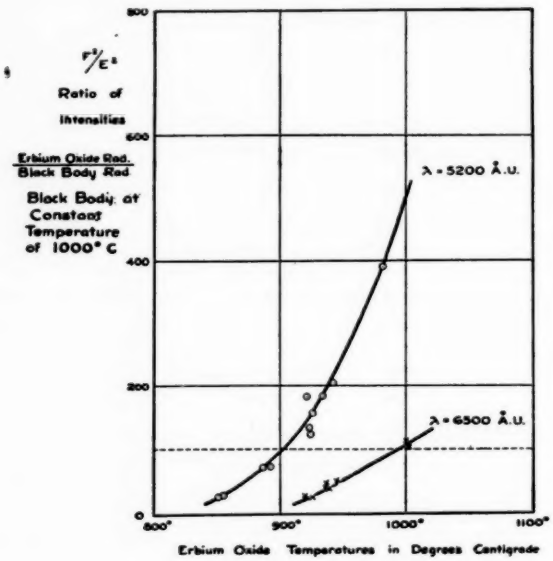

Fig. 3.

of the oxide. Observations were made in only two portions of the spectrum; in the red at wave-length .6500 μ and in the green at .5200 μ.

The results, which are plotted in Fig. 3 do not correspond quantitatively in all respects with the spectrophotometric determinations. That is because we happen to have to do in this experiment with a less intense selective radiator. Preparations of erbium oxide vary very widely in this respect. The radiating power, for example, is greatly lessened when the oxide is fused down in the electric arc. The bands are visible in such cases but at no wave-length does the radiation equal that from the furnace at the same temperature. Although the sample used in the test just described was obviously less active than that previously employed in the exploration of the spectrum, the green band attained at 900° a brightness equal to the corresponding region in the spectrum of the black body at 1000° and at 980° was four times as intense. The red band at 1000°, however, barely exceeded the black body radiation at that temperature.

SUMMARY.

(*a*) As a result of this investigation it seems certain that the peculiar banded emission spectrum of erbium oxide is due to the oxide itself and requires nothing more than a sufficiently high temperature to bring it out. The manner of obtaining this temperature seems to be of no importance.

(*b*) The emission bands at 1000°, especially in the green, are found to radiate much more strongly than a black body at the same temperature.

(*c*) The temperature at which the emission of the green bands equals that of a black body at 1000° is about 900°. This difference of temperature is much greater than that which could possibly have existed in the comparisons which were made under conditions where approximate equality of temperature was indicated.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY,
May, 1918.

EXPLANATORY NOTE.

Dr. Mallory's investigation was completed in the spring of 1918. The author, who had just been appointed to a professorship at Oberlin University, died suddenly of pneumonia, following an attack of influenza, before his paper was entirely ready for the press. I have completed it from his manuscript, retaining as far as possible the original form and point of view. His work, which was intended to be merely preliminary to a more general study of the emission of the rare earths, in its relation to purely thermal radiation and to luminescence, was interrupted by the untimely close of a career full of promise. It is however being continued by others who will endeavor to build upon the foundation which he laid, in loving recognition of the labors of a departed colleague.

If we accept a recent definition of luminescence, as radiation in excess of that which a body would emit by virtue of its temperature alone, and the well-known doctrine that thermal radiation of a given wave-length can never exceed that of a black body, the type studied by Mallory must clearly be designated as luminescence.

The make up of the spectrum as shown in Fig. 3 of his paper is strongly suggestive of luminescence. The complex group of overlapping bands in the blue which is suddenly developed as the temperature of 1000° is approached is very like those in the spectra of the phosphorescent sulphides as revealed by similar spectrophotometric measurements.[1] This phenomenon as it occurs in Erbium oxide, moreover, is strikingly

[1] Nichols, Proc. Am. Philos. Soc., LVI., 258, 1917.

similar to that described long since in the case of the oxides of calcium,[1] magnesium and zinc[2] where strong selective radiation in the blue of the spectrum appears at about the same temperatures. It is true that in these cases the effect is temporary, whereas in erbium oxide it appears to be permanent; but it may well be that in the latter instance the fatigue is so slow that it has not as yet been detected. Finally the rare earths are in general fluorescent and phosphorescent at ordinary temperatures and they are as subtly dependent in respect to their luminescent activity, upon mechanical and thermal treatment and crystalline condition as the sulphides and certain other phosphorescent materials. Thus different observers are likely to reach apparently discordant results according to the methods by which their materials are prepared. Taken all in all the evidence thus far appears to favor luminescence, superimposed upon ordinary thermal radiation, as an explanation of the phenomena described in Dr. Mallory's paper.—E. L. NICHOLS.

[1] Nichols and Crehore, PHYS. REV. (1), I., 161, 1894.

[2] Nichols and Snow, Phil. Mag. (5), XXXIII., 19, 1891.

ON THE RELATION BETWEEN THE K SERIES AND THE L SERIES OF X-RAYS.[1]

BY WILLIAM DUANE AND TAKEO SHIMIZU.

SYNOPSIS.—The object has been to measure both the emission and the absorption wave-lengths in the K and L-series characteristic of a chemical element (tungsten), using the same X-ray spectrometer throughout, to see if general relations among them could be found. Graphs have been drawn representing the ionization currents as functions of the crystal table angle. The peaks in these graphs corresponding to the lines α_1 (strong) and α_2 (medium) appear completely separated from each other, although the difference between their wave-lengths amounts to only 2.2 per cent. There is also faint evidence of a third (very weak) line, α_3.

A sharp drop in the absorption graph occurs near the γ line in the K-series corresponding to the K-critical absorption wave-length, and three sharp drops (a strong, a medium and a weak one occur near the L-series, indicating three critical absorption wave-length in that series. The critical absorption frequencies calculated from these graphs are, for the K-series: $\nu = 1.680 \times 10^{19}$; and for the L-series, $\nu_1 = .2438 \times 10^{19}$ (strong), $\nu_2 = .2773 \times 10^{19}$ (medium), $\nu_3 = .2917 \times 10^{19}$ (weak). The frequencies calculated from the peaks representing the emission lines are $\nu_{\alpha_1} = 1.437 \times 10^{19}$ (strong), $\nu_{\alpha_2} = 1.405 \times 10^{19}$ (medium) $\nu_{\alpha_3} = 1.39 \times 10^{19}$ (?) (weak). The precision of measurement is such that the probable error amounts to less than 1/5 per cent.

It appears from these data that to within 1/5 per cent. $\nu - \nu_1 = \nu_{\alpha_1}$ (strong), $\nu - \nu_2 = \nu_{\alpha_2}$ (medium) and $\nu - \nu_3 = \nu_{\alpha_3}$ (weak); in other words *each K α emission line frequency equals the difference between the K critical absorption frequency and one of the L critical absorption frequencies* to within the limits of experimental error. If this law, that *an emission frequency equals the difference between two critical absorption frequencies* applies to all emission lines we must assume critical absorption frequencies in the M series, etc. Two critical absorption frequencies lying between $\nu = 4 \times 10^{17}$ and $\nu = 5 \times 10^{17}$ taken together with those mentioned above will explain the presence of the β line in the K-series and six of the emission lines in the L series, etc.

1. In the analysis of X-rays about sixteen lines have been found to belong to the characteristic spectrum of each chemical element. Usually, although illogically, these have been divided into two series, the K series and the L series. The K series contains at least four lines, known as the α_1, α_2, β and γ lines, of which the γ line has the highest frequency. These four lines belong together in the sense that none of them can be produced by itself. As we increase the voltage V applied to the X-ray tube none of these lines appear in the spectrum until the voltage V reaches the value given by the quantum equation

$$Ve = h\nu, \tag{1}$$

[1] A paper read at the New York meeting of the Physical Society on March 1, 1919.

where e is the charge on the electron h Plank's action constant and ν, a frequency at least as high, and possibly slightly higher than that of the γ line. When the critical voltage has been reached, all four lines appear together; and their intensities increase in approximately the same ratio, if the voltage is raised still higher.[1]

The above is not true of the L series as a whole. In this series there are at least two and probably three groups of lines, the lines in each group being connected together in much the same way as are the lines in the K series.[2]

In the analysis of the X-ray absorption spectra of the chemical elements there appears to be only one critical absorption frequency connected with the K series. This frequency lies close to and probably slightly above that of the γ line. Within the limits of experimental error it equals the frequency that must be substituted in the quantum equation (1) to give the energy of the electron required to produce the K series.

In the absorption spectra of uranium, thorium, bismuth and gold De Broglie found three critical absorption frequencies characteristic of each element and in the neighborhood of its L series. The writers have found three such critical frequencies in the absorption spectra of both lead and tungsten. Doubtless these three absorption frequencies belong respectively to the three distinct groups of lines in the L series.

It appears, therefore, from purely experimental evidence that we may divide the known lines in the X-ray spectra of a chemical element into four groups, one in the K series and three in the L series, each group containing a critical absorption frequency and about four emission lines. The lines in each group are connected together in some way, but the relation between their frequencies is not given by the equation

$$\nu = \nu_0\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right)$$

in which ν_0 is a constant, and τ_1 and τ_2 are small whole numbers.

The question now arises: Is there any relation between the various groups of lines? Some years ago Kossel suggested that the difference between the frequencies of the α and β lines in the K series might be equal to the frequency of one of the strong lines in the L series, and considerable discussion on this point has appeared in the literature expecially in connection with the theories of the mechanism of X-ray emission spectra and of the structure of the atom. It is evident, however, that this relation cannot be a general relation, for there are many more lines in the L series than in the K series.

[1] See D. L. Webster, PHYS. REV., June, 1916, p. 599, and June, 1917, p. 571.

The authors have undertaken the research reported in this paper for the purpose of measuring both the absorption and the emission frequencies with the same apparatus, to see if a more general relation between the frequencies can be found.

We have used the X-ray spectrometer previously described,[1] with a calcite crystal, the formula for the wave-length λ being

$$\lambda = 2a \sin \theta = 6.056 \times \sin \theta \times 10^{-8} \text{ cm.}$$

where θ is the grazing angle of incidence. The X-rays passed through two narrow slits in thick lead blocks before striking the crystal thus obviating a large correction for the absorption of the X-rays in the calcite, as previously explained (*l. c.*). The X-ray tubes were of the Coolidge type, one of them having a tungsten and the other a molybdenum target.[2] The currents passing through these came from a high tension transformer with a system of condensers and kenotrons attached to it for producing approximately a constant difference of potential.

The curves in Fig. 1 represent the K lines of tungsten in both the first and second order spectra. The constant difference of potential applied to the tube amounted to about 100,000 volts in this experiment. The α lines were measured on both sides of the zero line of the spectrometer thus obviating a direct determination of the zero point. A correction of about 45″ of arc must be subtracted from the double grazing angle on account of the excentricity of the spectrometer scale.

There appears to be a somewhat better definition of the lines on the right hand side of the zero line than on the left. Doubtless this is due to a slight lack of uniformity in the crystal structure.

The two α lines on the right hand side appear to be completely separated from each other, even in the first order spectrum. This gives an idea of the precision with which the wave-lengths can be estimated, the difference between the two α wave-lengths being about 2.2 per cent. The position of each peak can be estimated to within 10″ of arc. Since the double grazing angles are about 4°, this means that the error of measurement is less than 1 part in 1,000, unless the same error is made on both sides of the zero line.

The peaks corresponding to α_2 are somewhat unsymmetrical, the slopes on the long wave-length sides being slightly more extended than on the short wave-length sides. This lack of symmetry suggests the presence of an additional line α_3 (?) close to and on the long wave-length side of α_2. Its wave-length should be about $.214 \times 10^{-8}$ cm. To the left of the β

[1] PHYS. REV., December, 1917, p. 624.

[2] Dr. W. D. Coolidge kindly sent us these tubes.

line appears a sharp drop in the curve. This marks the position of the critical absorption wave-length in the K series. The angular breadth of the drop about equals that of one of the peaks, namely 2′ of arc, and the angle corresponding to the center of the drop was used in calculating the critical absorption wave-length.

In this experiment the rays did not pass through an absorbing screen

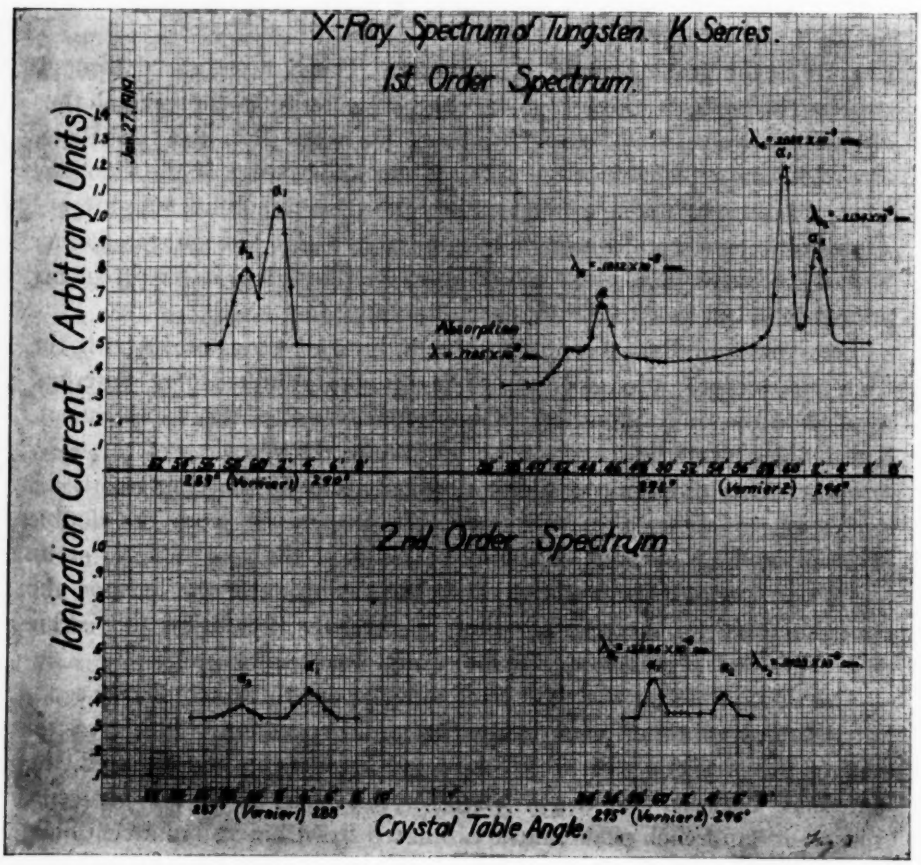

Fig. 1.

of tungsten outside of the X-ray tube, and the reason why the absorption drop appears in the curve is that we placed the X-ray tube in such a position that the rays passing through the spectrometer slits came from the target in a direction almost parallel to its surface. Under these conditions, since some of the rays are produced slightly below the surface of the target, part of them is absorbed by the surface layers of the target and by any irregularities there may be on the surface.

We have also measured the critical absorption wave-length in the K

series using an X-ray tube with a molybdenum target, and placing a layer of sodium tungstate between the tube and the spectrometer as an absorbing screen. In this way we obtained the following values for the wave-length: $\lambda = .1786 \times 10^{-8}$ cm. in the first order spectrum, and $\lambda = .1784 \times 10^{-8}$ cm. in the second order spectrum.

The critical absorption wave-lengths in the L-series of tungsten were measured as follows:

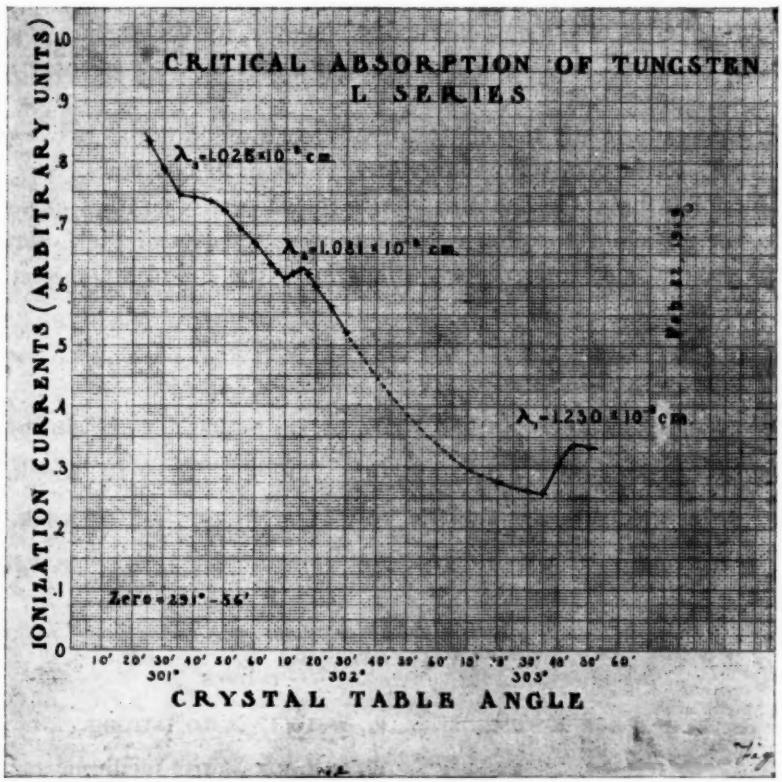

Fig. 2.

The curve in Fig. 2 represents the current in the spectrometer's ionization chamber as a function of the readings of one of the verniers attached to the crystal table in an experiment in which the X-rays came from a molybdenum target and passed through a *thin* layer of sodium tungstate before reaching the spectrometer slits. The three breaks in the curve correspond to the three critical absorption wave-lengths of tungsten that lie in the neighborhood of its L series of emission lines.

We determined the zero on the scale by taking readings on both sides

of the zero line. The value of the zero point given in the figure contains the correction for eccentricity.

The amount of X-ray energy that passes through the glass walls of the X-ray tube in the region corresponding to these long waves is quite small, and we, therefore, had to widen the spectrometer slits somewhat in order to measure the ionization currents. As a consequence the angular breadth of the drops in the curve have increased to four or five times the breadth of the drop in the K series curves. This has not increased the percentage error of the measurements, however, for the grazing angles of incidence in the L series are five to seven times as large as those in the K series.

In this experiment the constant difference of potential between the electrodes of the X-ray tube amounted to about 24,000 volts.

The following table contains the frequencies of vibration calculated from the critical absorption wave-lengths in the K and the L series of tungsten, and also from the wave-lengths of the α and β emission lines of its K series.

Critical Absorption Frequencies.

K Series	*L Series*
1st order spectrum $\nu = 1.680 \times 10^{19}$	$\nu_1 = .2438 \times 10^{19}$ strong,
1st order spectrum $\nu = 1.679 \times 10^{19}$	$\nu_2 = .2773 \times 10^{19}$ medium,
2d order spectrum $\nu = 1.681 \times 10^{19}$	$\nu_3 = .2917 \times 10^{19}$ weak.
Average $\nu = 1.680 \times 10^{19}$	

Emission Frequencies.

β-line	α-lines
$\nu_\beta = 1.628 \times 10^{19}$	$\nu_{\alpha_1} = 1.437 \times 10^{19}$ strong.
	$\nu_{\alpha_2} = 1.405 \times 10^{19}$ medium.
	$\nu_{\alpha_3} = 1.39 \times 10^{19}$ (?) weak.

In searching for a general relation between the emission frequencies and the critical absorption frequencies the idea immediately presents itself that an emission frequency may be the difference between two absorption frequencies. The fact that the L series contains three critical absorption frequencies, (a strong, a medium and a weak one), and that there are at least two α emission lines (a strong and a medium one), and possibly a third weak one, lends weight to the idea. From the frequencies contained in the above table we have

$\nu - \nu_1 = 1.436 \times 10^{19}$ (strong), $\nu_{\alpha_1} = 1.437 \times 10^{19}$ (strong),

$\nu - \nu_2 = 1.403 \times 10^{19}$ (medium), $\nu_{\alpha_2} = 1.405 \times 10^{19}$ (medium),

$\nu - \nu_3 = 1.388 \times 10^{19}$ (weak). $\nu_{\alpha_3} = 1.39 \times 10^{19}$ (?) (weak).

It appears from this data, that as a matter of fact *each α line frequency equals the difference between the* K *critical absorption frequency and one of the* L *critical absorption frequencies* to within the limits of experimental error.

If this law applies to all emission lines we must assume the existence of one and perhaps more critical absorption wave-lengths lying between $\lambda = 6 \times 10^{-8}$ cm. and $\lambda' = 7.5 \times 10^{-8}$ cm. (the M series) in order to explain the presence of the β-line in the K series. Two critical absorption wave-lengths lying in this M region taken together with the three critical absorption wave-lengths in the L series explain, according to the law, the presence of 6 of the lines in the L emission series.

The γ line in the K series and several lines in the L series lie very close to the critical absorption wave-lengths, and in order to explain them we must assume the existence of other critical absorption wave-lengths in the suspected N series, etc.

In conclusion we call attention to the fact that the equations which have been suggested to represent the lines in ordinary spectrum analysis are usually in the form of the difference between two functions, and also that X-ray critical absorption is not the same as ordinary absorption which obeys Kirchhoff's law.

HARVARD UNIVERSITY,
March, 1919.

THE VELOCITY OF SOUND AND THE RATIO OF THE SPECIFIC HEATS FOR AIR.

BY T. C. HEBB.

SYNOPSIS.—The ratio of the specific heats for air obtained from the author's determination of the velocity of sound does not seem to be as high as that obtained by different observers using the Lummer-Pringhseim method. This was thought at first to be due to experimental errors in the determination of the velocity of sound. A redetermination gives, however, a value very close to the previously determined value.

The cause of the discrepancy is found, however, to be due to the method of obtaining the velocity of sound for dry ir at 0° C. from observations made in air containing moisture. The usual transformation leaves out the term $\sqrt{\gamma_0/\gamma_m}$ where γ_0 is for dry air at 0° C. and γ_m is for air containing a certain per cent. of moisture. The term is small but not negligible. It can be calculated with sufficient accuracy.

The corrected values of the velocity of sound can then be used to determine γ for dry air at 0° C. The results obtained are very satisfactory.

SOME years ago I made a determination of the velocity of sound by a new method which seemed to give very accurate results.[1] At that time I was not interested in the ratio of the specific heats, and, hence, made no effort to calculate its value. The value of the velocity obtained at that time, however, has since been used by Moody[2] in his paper on the ratio of the specific heats; but he failed to correct for the fact that the ideal gas laws were used in its calculation. Even if this correction be applied the value of γ thus obtained is still lower than the value obtained by different observers using the Lummer and Pringsheim method. This is due to the fact that I failed to apply a correction which is necessary in obtaining the velocity of sound for dry air at 0° C. from observation made in moist air.

Now both of these corrections can be calculated, and, hence, it is of interest to see what value of γ is obtained by applying them. This paper contains an application of these corrections and also the account of a new determination of the velocity of sound. This determination was made two years ago and before I saw what was the explanation for the difference in value between γ as obtained by my velocity of sound and that obtained by the Lummer-Pringsheim method. I may forecast

[1] PHYS. REV., Vol. XX., No. 2, Feb., 1905.

[2] PHYS. REV., Vol. 34, No. 4, p. 275, 1912.

the results of the experiment by saying that the value of the velocity obtained is practically the same as that obtained in 1904.

1. Velocity of Sound.

The method used was the same as that used in my previous determination. The same apparatus was used which had been carefully preserved at Ryerson Physical Laboratory, University of Chicago, where the experiment was done. The method was of an interference type. Two coaxial paraboloids—5 ft. in diameter—had each a telephone transmitter. In one paraboloid the transmitter was placed in the focus, and in the other it was placed near the focus. Each transmitter was in series with a battery and one primary of an induction coil containing two primaries and one secondary. A telephone receiver was in series with the secondary of the induction coil. A source of sound was placed in the focus of the paraboloid, having a transmitter near its focus. This paraboloid was always kept stationary. If the other was moved, always keeping it coaxial with the stationary one, the sound in the receiver of the telephone passed through maximum and minimum values. By this means it was possible to measure the wave-length of the particular note used. And, as a single setting could be made with considerable accuracy, and, as it was possible to move the one paraboloid through a distance of 80–100 feet, it was possible to obtain the wave-length with an accuracy of about one tenth of one per cent., as was shown in my previous paper.

A whistle blown with a constant air pressure was used as a source of sound. This, although presenting difficulties, was the most constant source of frequency, with sufficient intensity, available. To insure constancy when observations were made, the whistle was kept in unison with a tuning fork of known frequency.

The experiment was performed indoors in a basement hall, and, hence, there were no wind disturbances. The temperature was determined by eleven thermometers spaced along the distance over which the observations were made. The dew point was determined with an Alluard hygrometer.

In my previous experiment I used only one frequency, owing to the fact that I had only one tuning fork of sufficiently high pitch. In this experiment, however, I had at my disposal a set of standard tuning forks. These forks, with the exception of the 4,096 d.v., had been kept in good condition. The one marked 4,096 d.v. had apparently been hit and dented with a sharp metallic hammer. On comparing the forks among themselves it was found that it was impossible to get beats due to com-

bination tones, excepting in the case of the 4,096 fork, which was found to have a frequency of 4,099.4 relative to the 2,048 d.v. fork. It was later found, however, that this fork could not be used as its frequency was too great.

In order to be sure that the absolute pitches of the forks were as marked, three of them were tested in the following manner. First, a fork with a frequency of about 100 was compared with a standard clock; and, second, the forks to be tested were compared with the standardized tuning fork.

In order to get the frequency of this intermediate fork, a stylus was attached to one prong so that it could make a trace on a smoked drum. By this means the period was found, (1) by direct comparison with the clock, and, (2) by comparison with a pendulum which had been compared with the clock. As the comparison took a great deal of time, the tuning fork was kept in vibration by means of an electromagnet between its prongs. This electromagnet was operated once a second from the clock circuit. This method resulted in an occasional phase change for which, however, correction was made. The results of five determinations are given in the following table:

TABLE I.

Method.	Time, Seconds.	t.	N_t.	N_{21}.
1. Clock.....	120	23° C.	99.817	99.839
2. "	120	21° C.	99.848	99.848
3. "	120	21° C.	99.812	99.812
4. Pendulum.....	106	32.2° C.	99.815	99.839
5. "	80	23.2° C.	99.800	99.824
			Mean.....	99.833

The probable error of the mean is .004.

To find the frequency of the forks to be directly used in the experiment, a high-frequency generator was used. On its shaft was fitted a switch which operated once for every revolution of the generator. This actuated an electromagnet which recorded on a revolving drum with the trace of the standardized fork alongside of it. The idea entertained at first was to get the note produced by a telephone receiver in series with the generator, in unison with that of the fork whose pitch was to be determined, and, then, calculate its pitch from the speed of the generator as obtained from the tracings on the drum. This did not succeed, as it was found to be impossible to keep the generator speed sufficiently constant to keep the two notes in unison. It was found, however, that it was possible to keep the generator-telephone note out of unison with

the tuning fork just enough to enable the number of beats in a certain time to be counted. Then, if the precaution was taken to be sure which frequency was the higher, it was possible to determine the relative frequencies. Table II. will make this clearer.

TABLE II.

Revolutions of Generator from Drum Record.	Corresponding Beats.	No. of Revolutions to Make Unison.	No. of Waves of Standard Fork.	Waves per Revolution.
279	30	278.34	869.0	3.1221
257	20	256.34	800.0	3.1212
214	20	213.34	665.4	3.1190
300	20	299.34	934.1	3.1205
219	20	218.34	680.97	3.1188
246	20	245.34	765.65	3.1207
			Mean.....	3.1204

In this case the generator-telephone note was higher than that of the tuning fork, and the rotor of the generator had 30 teeth. These results were obtained with the fork marked 960 d.v. It will be noticed that the number of beats is always the same. By the use of a switch in the circuit which recorded the revolutions of the generator it was possible to begin the record at any instant. Starting with the close of the switch 20 beats were counted and then the switch was opened.

Two other such determinations as given in Table II. gave means as follows:

$$\text{Means}_2 = 3.1199,$$
$$\text{Means}_3 = 3.1208.$$

The mean of these three means is 3.1204. The frequency of the 960 d.v. tuning fork, therefore, at 21° C. was:

$$N = \frac{30 \times 99.833}{3.1204} = 959.84.$$

As a check on these results the frequencies of the 1,024 d.v. and the 2,048 d.v. forks were determined in the same manner. The three means obtained for the 1,024 d.v. fork were:

$$\text{Mean}_1 \ldots\ldots\ldots 2.9250$$
$$\text{Mean}_2 \ldots\ldots\ldots 2.9247$$
$$\text{Mean}_3 \ldots\ldots\ldots 2.9253$$
$$\text{Mean} \ldots\ldots\ldots 2.9250.$$

The frequency of the 1024 d.v. fork was, therefore, at 21° C.:

$$N = \frac{30 \times 99.833}{2.9250} = 1023.93.$$

As only a single set of observations was made for the 2048 d.v. fork I include it in Table III. For this case the rotor of the generator contained 60 teeth.

TABLE III.

Revolutions of Generator Taken from Drum Record.	Corresponding Beats.	Number of Revolutions to Make Unison.	Number of Waves of Standard Fork.	Waves Per Revolution.
313	0	313.0	915.7	2.9256
457	50	456.17	1334.1	2.9246
491	30	491.5	1438.0	2.9257
213	20	212.67	621.8	2.9238
306	30	305.5	893.5	2.9247
667	20	666.67	1949.9	2.9248
442	50	441.17	1290.0	2.9240
			Mean.....	2.9247

Hence the frequency of the 2,048 d.v. fork was at 21° C.:

$$N = \frac{60 \times 99.833}{2.9247} = 2048.02.$$

These results show that the 960 d.v. fork was in error about .02 per cent.; the 1,024 d.v. fork about .01 per cent.; and the 2,048 d.v. fork was about correct. As the previous experiments had shown that the forks were consistent among themselves it was assumed from these results that all the forks were accurate at 20° C. It should be observed that all through this paper the following formula has been used:

$$N_t = N_0(1 - .00011t),$$

where N_t is the frequency of a fork at t° C. and N_0 is its frequency at 0° C.

With the frequencies known and the wave-length determined as indicated above, it was easy to get the corresponding velocity. The following table gives the results of my observations on page 78.

It will be noticed that only two results are given for the 3,072 frequency. No attempt was made to use it on August 11, and it was impossible to get any results with it on August 21. This was due to the fact that the reflected wave caused a change in the frequency of the whistle just as soon as the one paraboloid was moved. This caused trouble for all frequencies but the effect increased with the frequency. The trouble can be obviated by adjusting the air pressure supplied to the whistle. This is a long and tedious process and was not followed out on August 21. It was this reflected wave which made it impossible to use the 4,096 frequency.

An examination of the table reveals the fact that the mean velocity

Date.	Number of Waves.	Distance in Inches.	Temperature °C.	Dew Point °C.	Pressure Mm.	λ_t in Inches.	N_{20}.	V_t in Inches.	V_0 (Meters.)
Aug. 11	90	957.0	22.1	14	746.9	10.633	1,280	13,610	331.43
" 15	91	968.4	22.1	16	746.6	10.642	"	13,621	331.69
" 19	91	968.1	22.1	16.5	743.4	10.638	"	13,617	331.43
" 21	91	969.1	22.4	18.5	741.8	10.649	"	13,631	331.51
								Mean .	331.51
Aug. 11	108	957.5	22.1	14	746.9	8.866	1,536	13,618	331.62
" 15	109	964.9	22.1	16	746.6	8.8521	"	13,597	331.11
" 19	109	965.5	22.1	16.5	743.4	8.8582	"	13,606	331.16
" 21	109	966.4	22.4	18.5	741.8	8.8660	"	13,618	331.19
								Mean .	331.27
Aug. 11	144	956.3	22.1	14	746.9	6.6406	2,048	13,600	331.19
" 15	146	970.9	22.1	16	746.6	6.6499	"	13,619	331.64
" 19	145	963.5	22.1	16.5	743.4	6.6448	"	13,609	331.23
" 21	146	971.0	22.4	18.5	641.8	6.6507	"	13,621	331.26
								Mean .	331.33
Aug. 15	219	970.0	22.1	16	746.6	4.4292	3,072	13,606	331.33
" 19	218	967.0	22.1	16.5	743.4	4.4358	3,072	13,627	331.68
								Mean .	331.51

for a frequency of 1,280 is somewhat higher than the mean in the cases of the 1,536 and 2,048 frequencies. Frequencies of 960 and 1,024 were also tried, but it was found that they gave still higher values. This agrees with what was found in the previous experiment and appears to be related to the relative size of reflector and wave-length. Therefore, the results with the 1,280 frequency have not been used, although their addition does not affect the results seriously. The mean value of the velocity for the 1,536, 2,048 and 3,072 frequencies is 331.34 m. per second. This has to be corrected for the change in pitch due to the fact that the tuning forks were used at about 22.2° C., whereas they were correct at 20° C. The corrected value is, therefore, 331.26 m. per second, with a probable error of .05. This value is very close to the value obtained in my previous experiment, viz., 331.29. When, however, the correction given in the next paragraph is applied the agreement is not so close.

In calculating the results of Table IV. the relation

$$V_0 = V_m \sqrt{\frac{\rho_m}{\rho_0}}$$

was used where V_0 is the velocity in dry air at 0° C., V_m is the velocity as determined by the experiment, ρ_m is the density of the air at the time of the experiment and ρ_0 is the density of the air at 0° C. and at a pressure

equal to that at the time of the experiment. Now this formula assumes that the ratio of the specific heats for dry air is the same as that for moist air, which is not correct. The correct transformation should be obtained in this manner:

$$V_0 = \sqrt{\frac{p\gamma_0}{\rho_0}} \quad \text{and} \quad V_m = \sqrt{\frac{p\gamma_m}{\rho_m}},$$

where γ_m is the ratio of the specific heats for air at the time of the experiment and γ_0 is the ratio for dry air at 0° C.

Hence

$$V_0 = V_m \sqrt{\frac{\rho_m}{\rho_0}} \cdot \sqrt{\frac{\gamma_0}{\gamma_m}},$$

i. e., the results given in Table IV. should be multiplied by $\sqrt{\gamma_0/\gamma_m}$ in order to give an accurate result. As γ_0/γ_m is nearly equal to one we can calculate its value with sufficient exactness.

In order to do that consider a unit mass of a mixture of three gases—mono-, di- and triatomic. The three gases referred to are argon, oxygen and nitrogen as one gas, and water vapor.

Then $C_v = C_{v_1}m_1 + C_{v_2}m_2 + C_{v_3}m_3$, where the C_v's are the specific heats at constant volume of the mixture and individual gases respectively and m_1, m_2 and m_3 are the masses of the ingredients.

But $C_p - C_v = R$ for the mixture

$$\therefore \quad \gamma - 1 = \frac{R}{C_v}.$$

Where γ is the ratio of the specific heats for the mixture

$$\therefore \quad \gamma - 1 = \frac{R}{C_{v_1}m_1 + C_{v_2}m_2 + C_{v_3}m_3}$$

$$= \frac{R}{\frac{R_1}{\gamma_1 - 1}m_1 + \frac{R_2}{\gamma_2 - 1}m_2 + \frac{R_3}{\gamma_3 - 1}m_3},$$

where γ_1, γ_2 and γ_3 are the ratios of the specific heats for the three gases and R_1, R_2 and R_3 are their gas constants;

$$\therefore \quad \gamma - 1 = \frac{1}{\frac{1}{\gamma_1 - 1} \cdot \frac{m_1R_1}{R} + \frac{1}{\gamma_2 - 1}\frac{m_2R_2}{R} + \frac{1}{\gamma_3 - 1} \cdot \frac{m_3R_3}{R}}$$

But

$$\frac{m_1R_1}{R} = \frac{p_1}{p}, \qquad \frac{m_2R_2}{R} = \frac{p_2}{p} \quad \text{and} \quad \frac{m_3R_3}{R} = \frac{p_3}{p},$$

where p, p_1, p_2 and p_3 are the pressures of the mixture and the component gases respectively.

Therefore

$$\gamma = 1 + \frac{1}{\frac{1}{\gamma_1 - 1}\cdot\frac{p_1}{p} + \frac{1}{\gamma_2 - 1}\frac{p_2}{p} + \frac{1}{\gamma_3 - 1}\frac{p_3}{p}}.$$

It will be sufficiently accurate to use the theoretical values of γ_1, γ_2 and γ_3, *i. e.*, $= \gamma_1 = 1\frac{2}{3}$, $\gamma_2 = 1.4$ and $\gamma_3 = 1\frac{1}{3}$;

$$\therefore \quad \gamma = 1 + \frac{1}{3/2(p_1/p) + 2.5(p_2/p) + 3(p_3/p)}.$$

The per cent. of the gases at the time of my experiment were .95 for argon, 1.85 for water vapor and 97.2 for oxygen and nitrogen.

$$\therefore \quad \gamma_m = 1 + \frac{1}{3/2 \times .0095 + 2.5 \times .972 + 3 \times .0185},$$

where γ_m is the ratio of the specific heats for air with 1.85 per cent. of water vapor in it.

$$\therefore \quad \gamma_m = 1.4000.$$

If $p_3 = 0$, *i. e.*, if the air is dry

$$\gamma_0 = 1 + \frac{1}{3/2 \times .0095 + 2.5 \times .9905}$$

$$= 1.4015.$$

Hence

$$\sqrt{\frac{\gamma_0}{\gamma_m}} = \sqrt{\frac{1.4015}{1.4000}} = 1.00053.$$

Hence the corrected velocity of sound for dry air at 0° C. as obtained from these experiments is

$$= 331.26 \times 1.00053 = 331.44 \text{ m.p.s.}$$

It is of interest to correct my previous value of the velocity of sound. The value obtained was 331.29 m. per second. Now the average value of the water vapor for that experiment was 1.03 per cent.

Hence

$$\gamma_m = 1 + \frac{1}{3/2 \times .0095 + 2.5 \times .9802 + 3 \times .0103}$$

$$= 1.4007;$$

$$\therefore \quad \sqrt{\frac{\gamma_0}{\gamma_m}} = \sqrt{\frac{1.4015}{1.4007}} = 1.000285;$$

$$V_0 = 331.29 \times 1.000285$$

$$= 331.38 \text{ m. per second.}$$

If we give these two values of the velocity of sound equal weights we get for the mean:

$$V_0 = 331.41,$$

which appears to me cannot have an error of more than 2 or 3 centimeters.

2. The Ratio of the Specific Heats.

To calculate the ratio of the specific heats it is necessary to apply a correction to the formula $v = \sqrt{p\gamma/\rho}$ in order to take into account the deviation of air from the ideal gas law. This correction may be obtained in the following manner: An infinitely small adiabatic change may be expressed by the following equation—

$$C_p\, dT_p + C_v\, dT_v = 0,$$

where dT_p and dT_v are the changes in temperature when the pressure and volume are constant respectively. Their values can be obtained from the ideal gas law: $pv = RT$ and hence

$$Cp \cdot pdv + C_v vdp = 0.$$

In this equation C_p and C_v are the specific heats for an ideal gas. If, however, we determine the dT's from Van der Wall's equation then C_p and C_v will be the specific heats of the gas under consideration in so far as Van der Wall's equation represents the characteristics of that gas. Thus:

$$\left(p + \frac{a}{v^2}2\right)(v - b) = RT;$$

hence

$$dT_p = \left[\frac{p - \frac{a}{v^2} + \frac{2ab}{v^3}}{R}\right] dv$$

and

$$dT_v = \frac{v - b}{R} dp.$$

$$\therefore \quad C_p \frac{p - \frac{a}{v^2} + \frac{2ab}{v^3}}{R} dv + C_v \frac{v - b}{R} dp = 0.$$

$$\therefore \quad \gamma \left[\frac{p - \frac{a}{v^2 p} + \frac{2ab}{v^3 p}}{1 - \frac{b}{v}}\right] \times pdv + vdp = 0.$$

Now the term in the brackets is small and hence may be considered as a constant.

$\therefore$ pv^{γ_1} = a constant is the equation of the adiabatic for this gas, where

$$\gamma_1 = \gamma \left[\frac{p - \frac{a}{v^2 p} + \frac{2ab}{v^3 p}}{1 - \frac{b}{v}} \right].$$

As the term $2ab/v^3p$ is negligible in comparison with the rest of the expression under the brackets we get

$$\gamma_1 = \gamma \left[\frac{1 - \frac{a}{v^2 p}}{1 - \frac{b}{v}} \right].$$

Using the critical constants for air, viz., $T_c = -140°$ C. and $P_c = 39$ atmospheres we get for the expression in the brackets at 0° C. and 76 cm. pressure the fraction .99896.

$$\therefore \quad \gamma = \gamma_1 \times 1.00104.$$

Now γ_1 is obtained from the velocity of sound thus:

$$\gamma_1 = \frac{Vo^2 \rho_0}{P_{760}} = \frac{331.44^2 \times .0012928}{760 \times 13.5955 \times 980.616}$$

$$= 1.4017.$$

$$\therefore \quad \gamma = 1.4017 \times 1.00104$$

$$= 1.4031.$$

This is the value from the velocity of sound reported in this paper.

The value of γ obtained by using my previous value of V_0 as corrected in this paper, viz., 331.38 is

$$\gamma = 1.00104 \times \frac{331.38^2 \times .0012928}{760 \times 13.5955 \times 980.616}$$

$$= 1.00104 \times 1.4012$$

$$= 1.4026.$$

This value differs considerably from the value Moody obtained from my velocity of sound.

These two values of γ, 1.4031 and 1.4026, agree very well with the values obtained in recent years by the Lummer & Pringsheim method. This is shown in the following table, part of which is taken from Miss Shield's paper on the ratio of the specific heats of hydrogen.[1]

[1] PHYS. REV., Ser. 2, Vol. X., No. 5, p. 525, 1917.

TABLE V.

Observer.	Method.	
Lummer & Pringsheim	L. & P.	1.4025
Moody	"	1.4003
Partington	"	1.4034
Shields	"	1.4029
Hebb (1904)	Velocity of Sound	1.4026
Hebb (1919)	"	1.4031

The average of the two values of γ presented in this paper is 1.40285 and as I am of the opinion that the average of the two velocities of sound presented is accurate to 2 or 3 parts in 33,000, I am also of the opinion that this value of γ must be accurate to 2 or 3 parts in 14,000. This value, 1.40285, is almost identical with what one would expect from a theoretical standpoint. In the section on the velocity of sound it was shown that a gas consisting of .95 per cent. of argon and 99.05 per cent. of oxygen and nitrogen would have a ratio of the specific heats equal to 1.4015 considered as an ideal gas. If there be added to this the correction due to its deviation from an ideal gas, viz., .0014, there results the value 1.4029.

I wish to thank the staff of Ryerson Physical Laboratory for showing me every courtesy during the time I spent at the laboratory doing the experimental part of this work.

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